CHEMICAL TECHNOLOGY AND ANALYSIS

OF

OILS FATS AND WAXES

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BY

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EDITED BY

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WITH NUMEROUS ILLUSTRATIONS AND TABLES

PREFACE TO THE FIFTH EDITION

A SLIGHT delay in the publication of this volume is due to the lamentable death of Dr. Julius Lewkowitsch, which occurred within a few days of the appearance of the first volume of this edition of his *Chemical Technology of Oils, Fats, and Waxes.*

Such delay as has been unavoidable, owing to reorganisation, has not prevented the work from being issued in as new a form as possible ; on the contrary, it has given scope for the addition of the most recent data, of which due note has been taken, even up to the eve of publication.

Dr. Lewkowitsch had collected and annotated a very large amount of new material, including many personal observations of recent date, for incorporation in the second and third volumes.

It has been my privilege to edit these notes and bring the Work up to date, following on the lines laid down by the author so far as lies in my power.

My long association with Dr. Lewkowitsch in his analytical practice, extending over a period of seventeen years, has rendered the work a labour of love, and in the preparation of this volume no effort has been spared in order that it may present to the public a standard of completeness and excellence, which the author himself would have approved.

Notwithstanding this, it is only too probable that errors of omission have occurred and mistakes have crept in, and I shall be grateful to readers who will be so kind as to point out to me any such errors as may come under their notice. It should, however, be borne in mind that considerations of space and the desire not to render the volume too unwieldy have necessitated a very strict censorship over the available matter.

The physical and chemical characteristics of oils and fats in commercial use have been somewhat modified during the last years owing to improvements in preparing and refining the natural products. For

this reason, some of the older figures, published in the last edition, which obviously referred to badly refined or highly rancid specimens, have been eliminated.

Owing to the continuous search for new oils and fats, especially for edible purposes, the sources of supply are being widened, and some data regarding a number of little-known oils, which may in the future prove of commercial importance, have been added.

Under the headings of the individual oils and fats will be found a large number of hitherto unpublished observations obtained in this laboratory.

The subject-matter for Vol. III. is already in the press.

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CHAPTER XIII

COMMERCIAL PREPARATION OF THE RAW MATERIALS USED IN THE OILS, FATS, AND WAXES INDUSTRIES

Commercial Preparation of Oils and Fats

OILS and fats serve the human race as one of the most important articles of food. Hence operations having for their object the preparation of oils and fats date back to the remotest times in the history of mankind. The cave-dweller who first collected the fat dripping from the deer on the roasting-spit may be considered as the first manufacturer of tallow, just as the inhabitant of a tropical country who first collected the oil which ran off the broken kernel of the cocoa nut, on exposure to the sun, may be looked upon as the first manufacturer of vegetable oils or fats. The technical appliances used for the production of oils and fats range, therefore, from the simplest contrivances up to the very elaborate machinery in vogue at present. Some of the oldest methods still survive to-day, such as the extremely primitive processes employed in the production of palm oil, the expression of olives, the boiling out of blubber, etc., although they are rapidly being replaced by modern methods. The first supplies of vegetable oils and fats were, no doubt, obtained from fruits, such as those of the palm and olive trees. The oils were recovered in an exceedingly crude fashion, either by storing the fruits for some time in holes in the ground, when fermentation of the mass set in and the oil rose to the surface, or by boiling the fruit in water.

An advance in the manufacture was reached with the expression of oils from fruits in some kind of a rough press, exemplified by the packing of the fruit into sacks, and covering these with wood weighted by stones. A further stage was marked by the production of vegetable oils from oleaginous seeds; these were originally ground up between stones, as is still being done at present in East India. The latest development is indicated by the processes involving the extraction with solvents.

Since oils and fats are obtainable in all countries of the world, it will be readily understood that even the crudest and oldest methods are still in existence. The detailed consideration of these modes of manufacture lies beyond the scope of this chapter, and the reader

must be referred to the following chapter, in which, under the heading of each individual oil or fat, such processes are described. Nor is it intended to give an exhaustive survey of the subject and to describe in detail the more recently adopted manufacturing operations. We shall therefore only briefly glance at the stages by which the most advanced technical processes and appliances used in large scale operations have been reached.

The processes employed for the production of oils and fats divide themselves naturally into three groups :—

(1) Preparation of oils and fats by rendering, *i.e.* boiling out, with water or steam.

(2) Preparation of oils and fats by expression.

(3) Preparation of oils and fats with the aid of solvents.

(1) *Preparation of Oils and Fats by Rendering, i.e. Boiling out with Water or Steam*

A survival of one of the oldest methods of rendering *vegetable oils and fats* (still practised in Central Africa, Indo-China, and some of the South Sea Islands) by heaping up oleaginous fruits and broken kernels, allowing the contained oil to melt by the heat of the sun and collecting the exuding fat (see Chap. XIV. " Carapa Oil," " Caÿ Caÿ Fat ") is at present represented by the system of preparing Cochin oil (see Chap. XIV.) by boiling out the sun-dried or kiln-dried cocoa nuts with water.

Since for a process of this kind very simple machinery is required, the method has still some fascination for inventors, and even at the present day processes are being patented having for their object the boiling out of fruits with water or salt solutions,[1] so as to facilitate the separation of the oil from the pulp by gravitation. Processes of this kind have been patented by *Graham and Kellogg*,[2] *W. H. Gesner and A. R. Brandly*,[3] and by *Miguel del Prado*.[4]

Whereas the boiling-out process is of minor importance in the preparation of vegetable oils and fats (excepting " Cochin oil "), " rendering " is applied on the largest scale to the production of *animal oils and fats*. Formerly animal oils and fats were obtained by heating over free fire those parts of the animal which contained oil or fat, so as to cause bursting of the fat-containing cells. Not infrequently the tissue would burn on to the sides of the vessel and lead to the destruction of the fat, or the heated mass would even boil over and the fat run into the flue, whereby volumes of acrolein were sent into the atmosphere.

This rough-and-ready method of heating the adipose tissue of animals over free fire may be considered as extinct in properly equipped establishments, but it is still being practised in small works on the

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[1] The heating of fat-containing material with an oil or fat similar to that which it contains has been patented by Berliner (English patent 23,146, 1907 ; United States patent 878,930 ; German patents 197,725, 208,443 (see "Bonefat") ; French patent 383,231).

[2] German patent 109,239.   [3] French patent 357,329.

[4] French patent 365,187 ; cp. also Tanquerel, French patent 345,849 ; Acuña y Gomez de la Torre, French patent 403,015 ; Chap. XIV. " Olive Oil."

Continent (and even patents are still being taken out therefor [1]). The nuisance which follows in the wake of a manufacturing process of this kind has naturally led to stringent regulations on the part of the sanitary authorities.

Even the practice of "trying," *i.e.* rendering, the blubber of the whale, seal, and sperm whale (see below) on board the whaling vessel over free fire has become obsolete, and the modern practice is to deliver the blubber in as fresh a state as possible to the whaling establishments, where the oil is rendered in digesters (see below, Chap. XIV. "Whale Oil," "Seal Oil").

The rendering of tallow from the "rough fat" as it comes from the slaughter-house to the rendering establishment is nowadays carried out under such conditions that no objections can be raised from a sanitary point of view. The simplest and, in my own experience, a very effective method for obtaining tallow for technical purposes, is to place the rough fat in covered lead-lined vessels provided with steam coils, bottom outlet taps, a trap-door for charging the rough fat, and a wide outlet on the top through which any offensive vapours that may be given off are conducted through closed pipes to the chimney stack or fire grate.[2] Hot water is then run on to the fat, and steam turned on. After heating for a sufficient length of time, the steam is shut off, when the clear melted fat rises to the top. It can then be drawn off ready for use or into another vessel for further purification (see below, "Refining," "Bleaching"). The animal tissue, etc., still containing considerable quantities of fat, is again boiled up with steam after a few per cent of dilute sulphuric acid have been added, whereby the cell membranes are "cut," so that they more readily part with the remainder of the occluded fat. The function of the acid consists also in "breaking" the emulsion formed by gluey matter and fat.

This second operation yields a somewhat inferior kind of fat as regards odour and colour; the proportion of free fatty acids is, however, not increased thereby, since dilute sulphuric acid is incapable of effecting hydrolysis.[3]

The foregoing method yields sufficiently good raw material for **technical** purposes. Therefore processes (patented) involving the melting out of rough fat *in vacuo* are an unnecessary complication of a simple operation.

Since melting out of the rough fat over free fire has been classed amongst the noxious trades, a number of apparatus have been designed in which the tallow is melted in closed vessels under pressure. Such vessels—termed *digesters*—consist essentially of a vertical boiler provided with a false perforated bottom, and constructed to withstand a pressure of several atmospheres. Live steam is turned into the boiler below the perforated bottom on which the rough fat rests; at the elevated temperature the mass parts readily with its occluded fat, and in a shorter time than by steaming at the ordinary pressure. An

[1] Cp. German patents 217,278, 223,559 (F. Wirth and L. Wirth).
[2] Cp. French patent 382,745 (G. Talbot); cp. also English patent 8397, 1912.
[3] Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1903, 73; also Vol. I. Chap. II.

apparatus of this kind, designed many years ago by *Wilson*, is shown in Fig. 1 ; it has served as a prototype for a number of more or less complicated digesters now in use. They are especially employed for working up the residues left after rendering, at the lowest possible temperature, " premier jus," " lard," etc. (see " Edible Fats," p. 31, and Vol. III. Chap. XV.).

More primitive are the methods for obtaining fish, blubber, and liver oils.
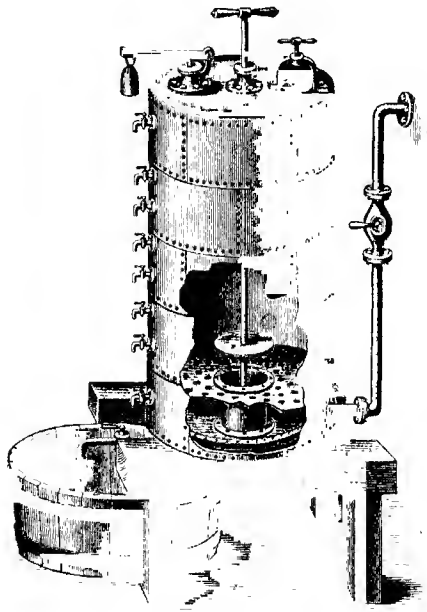
Fig. 1

The employment of digesters has found most extensive use in the enormous rendering establishments for tallow, bone fat, and lard, in the United States and South America (see Chap. XIV.), which in their turn have served as models for the rendering of blubber oils (see Chap. XIV. " Whale Oil "), fish oils (see Chap. XIV.), bone fat (see Vol. III. Chap. XV.), " Greases " (see Chap. XV. and Chap. XVI.), and all kinds of waste fats in slaughter-houses (see Chap. XVI.). Side by side with the processes using digesters, there are still in vogue, on a large scale, processes having for their object the boiling out of oil-containing material with the aid of water and steam in open vessels (see Chap. XIV. " Fish Oil," " Neat's Foot Oil ").

The preparation of animal oils and fats for edible purposes requires

special precautions, which vary with the special conditions which each individual material presents. A description of processes adapted to such special purpose will be found in Chapter XIV., under the headings " Lard," " Tallow," " Butter," " Cod Liver Oil," and in Volume III., under the heading " Margarine."

Apparatus designed for the continuous rendering (propulsion of the mass by screws, etc.) have proved useless, as after a very short time the moving parts become clogged up. A contrivance designed to avoid this drawback suggests introducing the rough fat into the melting vat from below.[1]

(2) *The Preparation of Oils and Fats by Expression*

The boiling-out process is, for obvious reasons, practically inapplicable in the case of small seeds, such as linseed and rape seed. The original method of obtaining the oil from such seed was most likely the same which is still used in most villages in India, viz. trituration of the seed in a mortar, so that the oil can exude. It may be safely assumed that the process of expression was applied in the first instance to the preparation of olive oil. The first woman who expressed oil by packing olives in a sack and weighting with stones may be considered the forerunner of the inventors of all the power presses that subsequently came into use. Pliny describes already in detail the apparatus and processes employed for obtaining olive oil by his Roman contemporaries, who used a simple screw press, a knowledge of which they had derived from the Greeks. In the East, where vegetable oils not only form an important article of food, but are also used for other domestic purposes, various ingenious applications of lever presses and wedge presses, and even of combined lever and wedge presses, have been employed from the remotest times. At an early stage of history the Chinese [2] employed the same series of operations which are followed in the most advanced oil mills of modern times, viz. bruising and reducing the seeds to meal under an edge stone, heating the meal in an open pan, and pressing out the oil in a wedge press, the wedges of which are driven home by hammers. This primitive process is still being carried out in the production of the soya bean cake and soya bean oil (see Chap. XIV. " Soya Bean Oil."), one of the staple industries of Manchuria. The remarkably good yields of oil which are thus obtained must be due to the length of time the meal is kept under pressure. The Japanese employed similar methods, and at the present time a special wooden wedge press—*tatsugi*—is largely employed in the oil industry of Japan. The olive press, which was also used in vineyards for expressing the grape juice (the wine press is supposed to be an Assyrian invention), found its way from the South to the North of France, and was commonly employed for the expression

[1] E. D. Miller, English patent 2806, 1900 ; German patents 212,797, 229,004, 247,322 (G. Honncke).

[2] The Chinese appear to have been the first to work up cotton seed for oil and cake. The seed was crushed some centuries ago in their native mills ; the oil was burned in their hand lamps and the cake was returned to the land as a valuable fertiliser.

of poppy, hemp, and rape seeds. The apparatus was then gradually improved, and thus were evolved the modern forms of the screw-press, next the Dutch or stamper press, and finally the hydraulic press.

With the screw-press, even in its most improved form, the amount of pressure practically obtainable is limited owing to the failure of its parts under the severe inelastic strain. Hence this form of press finds only limited application, as in the olive oil industry, for expressing the best and finest virgin oil, and in the production of animal fats for edible purposes, such as lard and oleo-margarine.

The Dutch or stamper press invented in Holland in the seventeenth century, was up to the early years of the nineteenth century almost exclusively employed in Europe for pressing oil seeds.[1] This press consists of two principal parts, an oblong rectangular box, with an arrangement of plates, blocks, and wedges, and over it a framework with heavy stampers which produce the pressure by their fall. The press box first consisted of strongly bound oaken planks, but later on cast-iron boxes were introduced. At each extremity of the box, a bag of oil meal was placed between two perforated iron plates, under which were a perforated bottom and channels for conducting away the expressed oil. Next were inserted filling-up pieces of wood, two of which— the speering blocks—were oblique or bevelled on one face, forming ways for the two wedges which pressed against them. Between the speering blocks, and separated also by a filling-in piece, were inserted the two wedges, one being the ordinary or driving wedge by which the pressure was applied to the seed bags, and the other an inverted or spring wedge, which was only driven down to loosen and free the various parts when the pressing operation was completed. The stamper which drove home the ordinary wedge was a heavy log of wood, about 16 feet long by 8 inches square, and it fell about fifteen times a minute through a maximum distance of 22 inches, by the action of a pair of cams fixed on a revolving shaft. When the pressure was deemed to have acted a sufficiently long time, the stamper suspended over the inverted wedge was brought into action ; by a single heavy blow it knocked the wedge out of its key-like position and thus freed the various parts of the apparatus for the removal of the pressed cakes.

This press has had to give way to the hydraulic press, although in some old-fashioned establishments in Holland the stamper press could still be seen at work in the 'eighties of the last century.[2]

The invention of the hydraulic press in 1795 by *Joseph Bramah*,[3] effected the greatest revolution in the oil industry, introducing as it did a new, easily controlled, and almost unlimited source of power ; the limit of the power being solely reached by the limit of the strength of the material the engineer is able to produce. Since then the hydraulic press has practically completely superseded all other appliances used for expression. In consequence of this epoch-making invention, assisted

[1] For a description of a prototype of this press, as used by the Chinese, cp. O. Vogel, *Chem. Zeit.*, 1913, 183.

[2] In 1818 Holland had 430, and in 1874, 536 oil mills.

[3] English patent, April 30, 1795.

as it was later on by the accumulator—invented by *William George* (later Lord) *Armstrong* (in 1843)—the seed-crushing industry reached a perfection of mechanical detail which soon secured to England the supremacy in this industry, at any rate up to the end of the last century.

The machinery required for the preliminary treatment of the fruit or seed must naturally vary with each particular kind of fruit or seed ; thus the preparatory operations for laying bare the fat-containing cells of cocoa nuts differ entirely from those necessary in the case of linseed.

A description of the special methods used for the expression of each individual oil and fat will be given in the following chapter. Here it must suffice to glance at the modern methods of preparing, crushing, and expressing the oleaginous seeds, as carried out in the best-equipped establishments.

Since the catalogues and advertisements of the engineering firms who make a speciality of this class of machinery supply excellent illustrations, it is not deemed necessary to reproduce them here, it being my intention in this work to lay greater emphasis on the chemical technology and general principles of the industries than on a full description of the machinery [1] used and the details of manufacturing operations.

The storage of the seeds requires special precautions. They must be kept dry, heaped loosely, and well ventilated ; absence of bright light is essential so as to prevent heating, especially if they be brought into the store-house in a moist state. When the seed is moist all conditions favourable to the action of enzymes (see Vol. I. p. 51) are given and hydrolysis of the oil or fat is produced with the formation of mono- and di-glycerides and of free fatty acids. (This is readily detected in the case of moist rape seed, as under favourable conditions the diërucin formed crystallises out from the oil.) The free fatty acids so formed are acted upon by the oxygen of the air, so that on pressing such seeds, oils are obtained, which not only contain free fatty acids, but also leave the presses in a rancid state.

The sequence of operations observed in treating oil seeds, oil nuts, etc., for the separation of the contained oils is at the present time as follows :—As a preliminary operation the oil seeds and nuts are freed from dust, sand, and other impurities, by sifting in an inclined revolving cylinder or sieving machine covered with woven wire, having meshes varying according to the size and nature of the seed operated upon. This preliminary purification is of the greatest importance ; it is especially indispensable for the preparation of edible oils and fats. In the case of those seeds which contain pieces of iron (nails ; hammer heads in the case of palm kernels), the seeds are passed over magnetic separators, which retain the iron. The seeds and nuts are decorticated [2] (where required), the shells are removed by mechanical means (sifters, blowers), and the kernels (" meats ") converted into a pulpy mass or meal by passing through a hopper over rollers, consisting mostly of five

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[1] Cp Lewkowitsch, Cantor Lectures on " Oils and Fats : their Uses and Applications," *Journ. Soc. Arts*, 1904.

[2] A. E. Box, English application 13,335, 1913.

chilled iron or steel cylinders, mounted vertically like the bowls of a calender (in older establishments stamping or crushing and grinding between stones in edge runners is still employed). These rollers are finely grooved, so that the seed is cut up whilst passing in succession between the first and second rollers in the series, then between the second and third, and so on to the last, until it is sufficiently bruised, crushed, and ground. The distance between the rollers can be easily regulated, so that the seed leaving the bottom roller has the desired fineness.

The suitably comminuted mass, forming a more or less coarse powder (" meal ") is either expressed at the ordinary temperature, or subjected to preliminary heating, the latter depending on the quality of the product to be manufactured. For the preparation of edible oils and fats, the mass is packed in bags and expressed in hydraulic presses *in the cold*, under a pressure of 300 atmospheres or more (*i.e.* a pressure of two tons or more to the square inch), so that the oil may exude readily. Such oils and fats are known as *salad oils, cold-drawn oils, cold-pressed oils* (see Vol. III. Chap. XV. " Edible Oils "). Under these conditions the oils and fats dissolve the smallest amount of colouring matters, and suffer in the least degree as regards quality. Obviously only a portion of the oil or fat contained in the fruit or seed is obtained in this manner ; a further quantity is gained by expression at a somewhat elevated temperature, which is reached by warming the seed previous to expression. The quality of the oil or fat naturally suffers when expressed in the hot, more of the extractive substances being dissolved in and intermixed with the oil. The taste also suffers ; the oil thus obtained is hardly suitable for edible uses and is chiefly employed for manufacturing purposes. The oil or fat which is retained by the press cakes can only be recovered by again comminuting the latter and subjecting the meal so obtained to a further expression.

In the case of oleaginous seeds of somewhat low value, such as linseed, cotton seed, the aim is to express in one operation the largest possible quantity of oil. Hence the broken seed is generally warmed in a steam-jacketed kettle, fitted with mixing gear, by passing steam into the jacket, and sending at the same time some steam through a " rose," fixed inside the kettle, into the mass while it is being agitated. This practice is a survival or rather persistence of the older method of moistening the seed with a little water while the seeds were bruised under an edge runner, so as to raise the temperature, and facilitate the bursting of the cells. The assumption that the albuminous mass is thereby coagulated [1] hardly holds good, the object being merely to warm the seed to a higher temperature and at the same time to moisten it, so that the cells part more freely with the imprisoned oil.

[1] K. Oga patents in English patent 4262, 1911, a method of exposing the comminuted material to a current of hot air, the temperature of which is so regulated that the albuminous matter does not coagulate. P. Schneider patents in French patent 432,787 the application of superheated steam (patented also by R. S. Woodward, jun., in United States patent 843,983, February 12, 1907) to the seeds before crushing. Cp. also the same patentee's earlier French patent 372,566, as also his English patent 15,961, 1911. Cp. also F. Wolfenden, United States patent 1,012,312.

The heated meal is then either packed by hand as is being done largely in the South of France in " scourtins " (bags made of plaited aloe leaves or cocoa nut leaves, camel hair or horse hair), or delivered through a measuring box, which is combined with an automatic moulding machine, into woollen bags or open cloths (as is done where the Anglo-American press is used), so that the preliminary pressed cakes can be put at once into the hydraulic press, in which the meal is sub-

jected to high pressure. In the latest constructions of cage presses (see below), the use of bags is entirely dispensed with, a measured-out quantity of seed falling direct into the circular press cage, and being separated by a circular plate of sheet-iron from the material which is to form the next cake.[1]
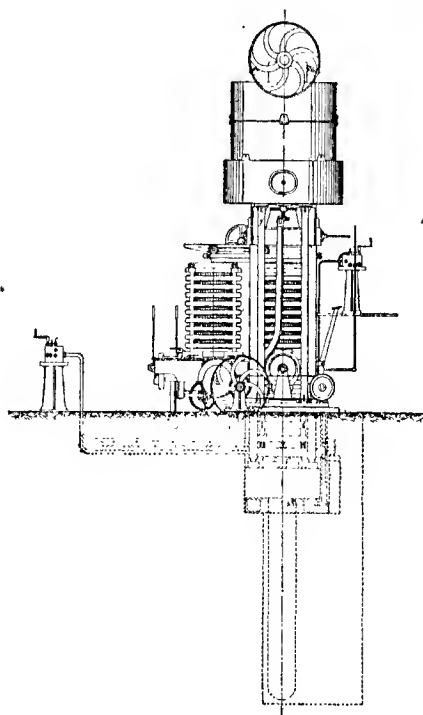
The essentials for proper oil pressing are a slowly accumulating pressure, so that the liberated oil may have time to flow out and escape ; a pressure that increases in proportion as the resistance of the material increases, and that maintains itself as the volume of material decreases through the escape of oil.

[1] Cp. E. C. Bisbee and C. F. Elmes, French patent 335,444.

Numerous forms of hydraulic presses have been devised. They may be divided into vertical and horizontal presses. Horizontal presses have practically ceased to be used in this branch of industry.[1]   At present vertical presses are almost exclusively in vogue.

The most primitive form of vertical press, and one which is still used where high pressure is not essential, is a drum or a box press, so called because on the platten are placed two circular metal tubes, one within the other, the inner being perforated throughout for the escape of the oil.   At the top of the press is secured a strong metal plate or table, having the same diameter as the inner box.   When the ram carrying the box is forced up against the surface of this table the seed is pressed. The seed bags, separated by metal plates, are deposited within a perforated box.   Experience, however, has demonstrated that the best presses are those provided with separate trays or seed boxes for each bag, and the ordinary oil press of this type is fitted with 4 to 6 seed boxes, and presses 4 to 6 separate cakes at one working.   A convenient form was the double oil press of *Blundell*, which admits of continuous working, one division being under pressure while the other division is being emptied and recharged.   This press has been practically ousted from the market by the following three types of presses :—

1. *The Marseilles Press.*—This press, a "pack press," dispenses with bags, seed boxes, and hair mats, the seed being packed by hand in "scourtins," to the number of 16 to 25 for one charge, the "scourtins" being simply separated in the press by corrugated iron plates.   This press is still largely used in the South of France, although the packing requires more manual labour than in the case of the Anglo-American press (see No. 2).   Moreover, this press offers inconvenience in keeping the bags straight, and the pressure cannot be raised to the same height as can be done in the following two types of presses.   In fact, the extreme limit of pressure is 250 to 300 atmospheres (34 to 40 cwts. per square inch), this being the limit of the resistance of the "scourtins." [2]

2. *The Anglo-American Press.*—This vertical press is at present the one mostly in use.[3]   It consists of an open press fitted with a number of iron press plates (from 10 to 16) between which the cakes are inserted by hand.[4]   The pressure employed in working with these presses is usually 2 tons per square inch.

3. *Cage Press* (*Clodding Press*).—This is a hydraulic press provided with a circular box or cage, into which the meal is filled as described above.   The box (cage) is either constructed of metal staves (see Fig. 4) (vertical steel bars), held together by a number of steel rings, or consists of one cylinder having a large number of perforations.   The presses of this class, which have perforated cylinders, although presenting

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[1] For a new horizontal press see, however, H. A. Herr, United States patents 801,872, 819,996, and *Journ. of the Franklin Institute*, 1909, 275.

[2] For an illustration of the Marseilles press cp. *Technologie et analyse chimiques des huiles, graisses et cires*, par J. Lewkowitsch, traduit par E. Bontoux.   Vol. ii. 575.

[3] A. Austerlitz (French patent 381,350, first addition 9347, and English patents 10,860, 1907 ; 7224, 1908) claims to obviate certain drawbacks to this press.   United States America patent 992,534.

[4] R. Koeber and S. Koeber patent in English patent 16,827, 1906, plates having on all four sides rigid raised edges with an inwardly inclined surface.

mechanically a more perfect arrangement, are not preferable to the cage presses formed by staves, as the holes easily become clogged up by the meal, when it becomes necessary to clean out the cylinder, an operation which involves a good deal of labour. To reduce the drawback caused by the clogging up of the holes, they are bored, in more recent constructions, conically, the diameter on the outside of the cylinder being larger than the diameter of the holes in contact with the cakes.

In order to save time and to obtain an increase of output with a given number of Marseilles or cage presses, each set (battery) of presses is provided with a preliminary (preparatory) press, in which the meal bags are compressed under a pressure not exceeding 15 to 20 cwts. per square inch. The shrinkage in volume caused by the outflow of oil is made up by bags containing fresh meal.

When the presses are charged the hydraulic pressure from the accumulator, and finally from the hydraulic pump, is allowed to act on the ram. The hydraulic ram then compresses the cakes, whilst the exuding oil flows down the sides in the case of the open presses (1 and 2), or through the openings between the staves (clodding presses), or through the perforations of the cylinder, as the case may be, into a tank below. After releasing the pressure, the cakes are taken out; the edges, which are naturally richer in oil than the bulk, and hence are soft and friable, are trimmed off in a paring machine.[1]

Oil obtained from heated meal is usually more highly coloured and harsher to the taste than cold-drawn oil, since larger quantities of the extractive substances (albuminoids, mucilaginous substances) are dissolved in, and intermixed with, the oil. According to the care exercised by the manufacturer in regulating the range of temperature through which the seed is heated, various grades of oil are obtained.

When the seeds contain large amounts of oil, exceeding 40 per cent (palm kernels, cocoa nuts, castor seeds), it is necessary to repeat the process of expression. This is done by breaking up the cakes in a cake-breaking machine, reducing them to meal in an edge runner, and subjecting the meal to a second expression in the manner described already.

In the case of some oil seeds which contain more than 40 per cent of oil (arachis, sesamé) the first expression in bags leads to difficulties, as the oily meal causes " spueing," i.e. the meal exudes and escapes from the presses together with the oil.

Hence in modern installations the first expression of these seeds is carried out in " clodding " presses. These presses, generally worked in sets of two, or three, or more, have a seed kettle fixed on the top of the press (see Figs. 2 and 3); the kettle is provided with one or more openings, corresponding to the chamber or chambers in the heads of the press or presses. These chambers can be closed at the top and bottom by slides, actuated by levers, and are designed to contain as much meal as is required to form one cake. The measured charge of meal is then allowed to fall into the press box and is covered with a

[1] A. Austerlitz, in German patent 184,979 patents a special paring machine.

circular metal plate. This operation is repeated until the press is full, when hydraulic pressure is applied, and a ram forces the box against a sliding block at the head of the press. The oil exudes, and the meal is pressed into circular cakes ready for the second expression. After releasing the pressure, and removing the sliding block, the cakes are forced out by the hydraulic ram. They are then comminuted, and the meal is subjected to a second expression in a Marseilles or Anglo-American hydraulic press.

The mechanical part of the process has been improved recently,
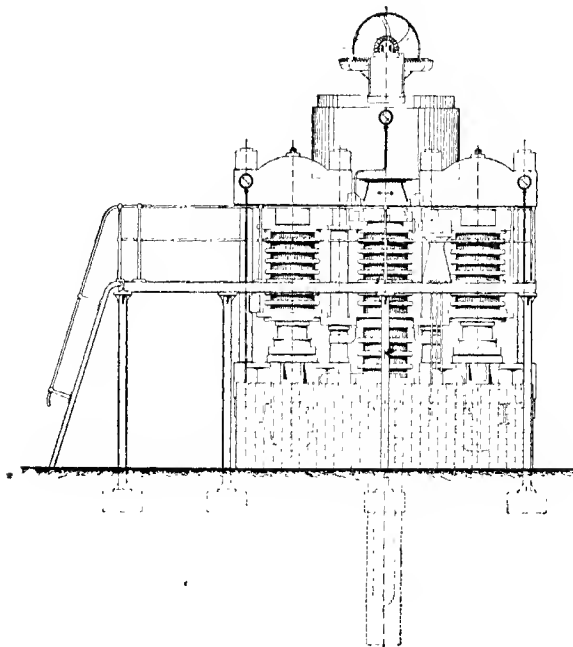
Fig. 3.

so that even for the second expression the open Anglo-American press can be dispensed with. The finishing presses are made of the same type as the press in which the first expression is carried out, and by making the press cages removable the pressing operation approaches an almost continuous one. These cages can be transported by means of a power-driven carriage (see Fig. 4) to the finishing presses; where one preliminary press is combined with two finishing presses to a battery, the cages can be conveyed into the adjoining finishing press by a swinging arrangement (see Figs. 5 and 6), their place being filled immediately by a charged cage, or by a cage containing finished cakes. Thus, with the exception of the time required for withdrawing the pressing cages and replacing them, the work goes on practically continuously. Further

advantages are offered by these presses in that the cakes require no paring, and that a saving of " scourtins " or press cloths in comparison with the Marseilles or Anglo-American systems is effected.

In the cage presses a higher pressure can be employed, and hence more oil can be obtained from the meal than in the open types (the Marseilles and Anglo-American presses). The pressure can be run up in practice from $2\frac{1}{2}$ to $2\frac{3}{4}$ tons per square inch. If the open presses could be made to withstand the same high pressure, they would undoubtedly yield the same amount of oil.

Cage presses having perforated cylinders (see above) are designed for still higher pressures, and installations have been erected during
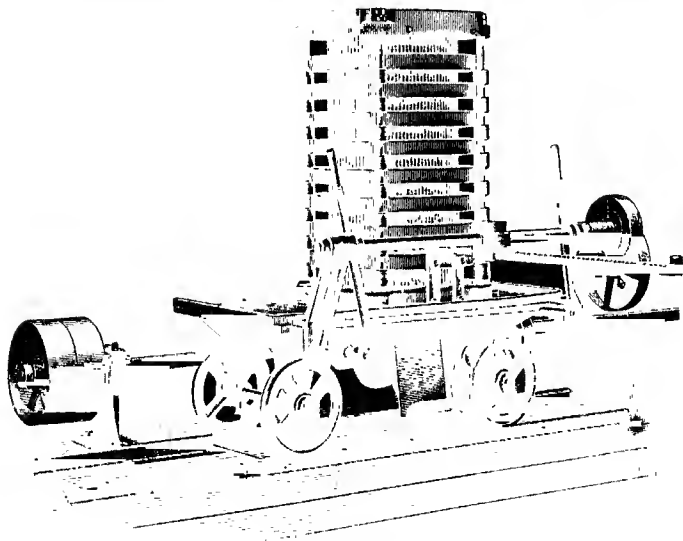
Fig. 1

recent years in which the pressure (under the piston) amounts to 450 atmospheres (3 tons per square inch), and even 600 atmospheres (4 tons per square inch). In order to provide for a ready outflow of the oil the number of holes in a cylinder of 420 millimetres diameter and 1400 millimetres height has been increased to almost 60,000. It should, however, be pointed out that no advantage is gained over the open presses or cage presses fitted with staves by these very high pressures. True, the cakes retain only about 7 per cent of oil, but stock-raisers prefer cakes containing 10 per cent of oil (excepting cakes made from undecorticated cotton seed).

In addition to the drawbacks mentioned already (cp. p. 5), the high prime cost of installing these expensive presses must militate against them. It has been ascertained in practice that the working expenses and the yield of oil of equal quality are almost identical in

installations of the older types and in mills having cage presses working under these extremely high pressures, whilst the initial outlay for these latter presses is from three to four times higher. Moreover, the oil produced under the higher pressure is more turbid than oil
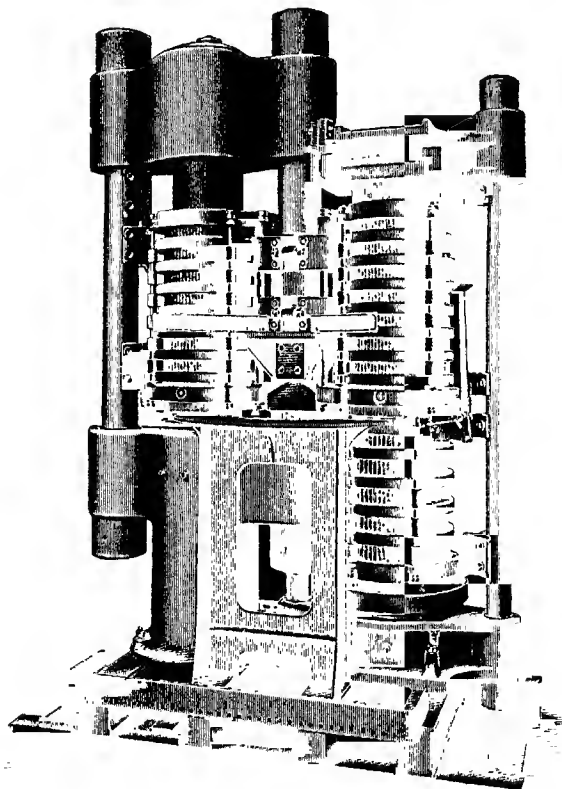
FIG. 5.[1]

obtained in the older types of presses, and is more difficult to clarify. This is no doubt due to a larger amount of extractive substances having passed into the oil.

Therefore the alleged advantages claimed for these presses have not been borne out, so far, in practice.

[1] The illustrations Figs. 2-6 have been engraved from drawings and photographs kindly lent by Messrs. Greenwood and Batley, Leeds.

It should be noted that the figures given above for the pressures represent the pressures under the press piston, as read off the manometer. They by no means indicate the pressures on the cakes themselves. As a general rule it may be accepted that the cakes are under a pressure of about two-thirds of that indicated by the manometer.

The oil flowing down the sides of the press or through the staves or holes is caught in reservoirs placed below the level of the floor and
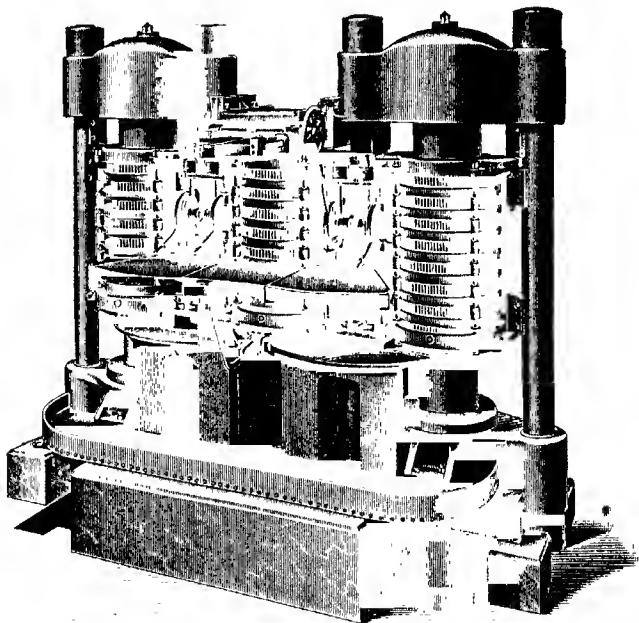
Fig. 6.

is pumped into store tanks for settling, clarifying, and refining (see below).

Although the modern presses described above work economically, still the obvious drawback adheres to them that the work is not entirely continuous. This feature has induced, at an early period, several inventors to design continuously working presses, such as those of *Bessemer and Haywood*,[1] *Müller*,[2] *Bergreen*.[3] But not one of these

[1] English patent 1261, 1849.   [2] German patents 26,343, 1883 ; and 35,781, 1889.
[3] German patent 65,165, 1892.

presses has been able to maintain itself in practice owing to the high cost required for power, in conjunction with a very small output.

Recently experiments were made in several European oil mills with an automatic press, designed by *V. D. Anderson.*[1] In this press the seeds are introduced through a hopper and carried forward, by means of screw blades, into a horizontal cage formed by metal staves. The spirally arranged blades do not set the mass in rotation, but subject the seeds to a force of torsion by contact with the mass in front of them. The expressed seed is driven on to the end of the horizontal cage, and as soon as a certain pressure is exceeded a portion of the expressed mass is discharged. This press works on cold seed only, and therefore the oil which is obtained is of very good quality.[2] The press is especially recommended by the inventor for linseed, rape seed, and cotton seed. His claim that only 5 per cent of oil are left in the ejected mass has, however, not been borne out by experiments with which the author is acquainted. Thus, in the case of cotton seed, the pressed material still contained 7 per cent of oil, although the pressure amounted to 5 tons per square inch, whereas the same material pressed in a hot press of the Anglo-American type yielded cakes retaining 4 per cent of oil only. The comparatively small output, the high cost for power, and the strongly corroding action which the compressed mass exerts on the metal constitute such serious drawbacks that it is very unlikely that this press will displace the above-described hydraulic presses. Even recent improvements embodying the application of much harder steel (such as high-class tool steel) have not materially assisted in bringing this press into more extended use.

A press similar in design to the press constructed by *Bergreen*, in that it exhibits the same conical shape of the press chamber and the same general arrangement, has been patented by *F. C. Caldwell.*[3] The press differs, however, from *Bergreen's* in that the screw blades, which in the latter's press are arranged spirally on a vertical shaft, are replaced by spiral corrugations, or screw threads, which extend approximately half-way around the solid vertical roller, whilst at the lower end the corrugations extend entirely around the roller. The walls of the pressure chamber are formed by staves (as in cage presses) permitting the passage of oil. The author has had no practical experience with this press, which is stated by the inventor to be particularly applicable to cotton seed and linseed.

V. J. Lauermann,[4] claims an apparatus for the extraction of cotton seed and other oil seeds, consisting of a vertical jacketed cylinder, inside which a shaft provided with arms rotates. These arms are fitted with knives running parallel to the shaft, and almost touching the wall of the cylinder. There are also fixed knives inside the cylinder. The seed is crushed on passing through the cylinder.

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[1] Cp. United States patents 960,143, 960,144.
[2] Cold-pressed linseed cake is liable to evolve prussic acid (see "Linseed Oil," Chap. XIV.), hence cold pressed cake must not be used as cattle food.
[3] English patent 8696, 1905.
[4] United States America patent 876,363 ; English patent 16,642, 1908.

Under this head may also be mentioned the attempts that have been made to use hydro-extractors in the ordinary routine of oil mill work. They are, however, entirely unsuitable for this purpose. Recently, experiments have been made both in Algiers[1] and California[2] to extract, in the first instance, an edible oil from freshly gathered olives by centrifuging the fruit. Nothing definite can, however, be stated as to the advantages alleged to have been obtained, and the reader must therefore be referred to the original publications mentioned in the footnotes.

Hydro-extractors can only be employed with advantage for subsidiary operations in the oil and fat industries, such as for separating the oil from the meal which has exuded through the cloth, or generally from by-products rich in oil.

For the application of centrifugals[3] to the recovery of fat from milk, see " Butter Fat."

For a process of extracting olive oil from the fruit by diffusion see " Olive Oil."

The extraction of oils and fats *in vacuo* has been patented by *W. S. Simpson*,[4] cp. also " Olive Oil."

The analytical control of this technical process confines itself chiefly to the determination of the proportion of oil or fat contained in the raw material—oleaginous seeds—and the determination of the oil left in the expressed cakes. For these estimations, quantities of not less than 100 grms. should be used.

The sample is prepared for analysis by disintegrating it carefully in a suitable manner, as by means of a cake-mill or coffee-grinder,[5] and exhausting it with ether, or petroleum ether, or carbon tetrachloride,[6] using any of the extracting apparatus described (Vol. I. Chap. IV.). The disintegration of the seeds requires great care, as otherwise considerable quantities of oil or fat may remain in the meal. The breaking up of the cells which occlude the oil or fat is best assisted by grinding with ignited sand, which offers the double advantage of breaking the cells more completely than is done by mere pounding in a mortar, and of presenting a large surface to the extracting solvent. In the case of seeds containing large quantities of oils and fats, it is advisable first to break up the mass roughly and to extract a portion only of the oil or fat, then to triturate the partially extracted mass with sand and finally exhaust completely. This specially applies to soya beans, copra, palm

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[1] Cp. L. Dugast, *L'Industrie oléicole*, Paris, 1905. p. 78 ; French patent 397,203 (Morel-Revoil) , French patent 411,493 (Sagols).

[2] *California Olive Oil , its Manufacture* By G. W. Shaw, College of Agric., Agr. Expt. Station, Bull. No. 158, Sacramento, p. 26.

[3] Especially those constructed by the Actiebolaget Separator, Stockholm.

[4] English patent 4661, 1910 ; French patent 141,970 ; United States patent 1,012,572.

[5] With regard to errors caused by deviating from these directions cp. *Journ. Soc. Chem. Ind.*, 1895, 447.

[6] Biltcryst, *Bull. de l'Assoc. Belge*, 1897 (10), 406.

kernels, and generally to all seeds containing more than 50 per cent of oil or fat.

If ether, or carbon bisulphide, or chloroform be employed, it is necessary to dry the material prior to extraction, moist seeds or cakes being apt to yield to the solvent non-fatty substances. Ether must first be purified ; this is best done by washing with water, in order to remove any alcohol, then drying over calcium chloride, and distilling off ; finally the ether is distilled over metallic sodium, in order to free it from the last traces of water and alcohol.

The drying of seeds or cakes containing drying oils, such as linseed and linseed cake, or even semi-drying oils, such as maize and soya oil, requires some care ; if the material has been dried at too high a temperature, or for too long a period, the drying oils refuse to pass readily into solution. This fact is clearly brought out by some experiments recorded in the following table due to *Klopsch* : [1]—

Linseed Cake.				Oil. Per cent
Dried 3 hours at 94°-96° C. gave	.	.	.	8·97
Dried 6 hours at 100° C. gave .	.	.	.	8 55
Dried 12 hours at 94°-96° C. gave	.	.	.	7·89

If the cakes have been dried at too high a temperature, brown resinous extracts (containing oxidised acids) are obtained. An analysis can therefore only be looked upon as correct if the extract has the appearance of a clear oil.

If petroleum ether or carbon tetrachloride [2] be used as a solvent, the drying of the material may be omitted. The petroleum ether must boil completely below 80° C. This solvent is specially suitable for the extraction of cakes containing drying oils ; moreover, it extracts much smaller quantities of non-fatty substances than ether does.[3]

Frequently the examination of the extracted oil is required ; this is done by the methods described in Vol. I. The microscopical examination of the meal will frequently afford valuable assistance.[4]

A large number of analyses of seeds and oil-cakes have been published by various observers.[5] A record, or even a summary, of such analyses obviously falls outside the scope of this work. I will therefore quote only some analyses by *Nördlinger* [6] as throwing light on the proportion of neutral oil to free fatty acids.

[1] *Zeits. f. analyt. Chem.*, 1888, 452.
[2] Cp. also Harding and Nye (*Journ. Ind. Eng. Chem.*, 1912 (4), 893).
[3] Cp. also B. Schulze, *Landw. Versuchsst.*, 1911 (75), 185.
[4] Cp. *e.g.* E. Collin, *Annales de chimie analytique*, 1909, 256.
[5] Cp. König, *Die menschlichen Nahrungs- und Genussmittel.*
[6] *Journ. Soc. Chem. Ind.*, 1890, 422.

[TABLE

Seeds	100 parts contain		Free Fatty Acids in Total Fat.
	Free Fatty Acids.	Total Fat.	
			Per cent.
Rape (*Brassica rapa*)	0·42	37·75	1·10
Cabbage (*Brassica campestris*)	0·32	41·22	0·77
Poppy (*Papaver somniferum*)	3·20	46·90	6·66
Earthnut (*Arachis hypogæa*)—			
(a) Seed	1·91	46·09	4·15
(b) Husks	1·91	4·43	43·10
Sesamé (*Sesamum orientale*)	2·21	51·59	4·59
Castor (*Ricinus communis*)	1·21	46·32	2·52
Palm nut (*Elæis guineensis*) with 6 per cent husks	4·19	49·16	8·53
Copra (*Cocos nucifera*)	2·98	67·40	4·42

Cakes.	Number of Samples.	100 parts contain		Free Fatty Acids in Total Fat.
		Free Fatty Acids	Total Fat.	
				Per cent.
Rape	6	0·93	8·81	10·55
Poppy seed	10	5·66	9·63	58·89
Earthnut (*Arachis*)	20	1·42	7·65	18·62
Sesamé	15	6·15	15·44	40·29
Palm nut	38	1·47	10·39	14·28
Cocoa nut	5	1·31	13·11	10·51
Linseed	2	0·75	8·81	9·75
Castor	10	1·27	6·53	20·07

The total fat was obtained by extraction with petroleum ether, and the free fatty acids were titrated with standard alkali and calculated to oleic acid.

The ratio of total fat to fatty acids is not necessarily the same in the cakes as in the expressed oils. Thus the " first-expressed " oils (" salad oils ") contain far less free fatty acids than does the total fat in the seeds. Consequently more free fatty acids remain in the cakes. The oils from the second and third pressings are richer in free fatty acids, but a large portion thereof remains behind in the cakes.

The following example will illustrate this :—

100 Kg. of Poppy Seed yielded	Oil. Per cent.	Containing Free Fatty Acids. Per cent.
Extracted with solvents.	46·9	6·82
Expressed—(a) Salad oil	39·0	1·92
(b) Commercial oil	2·5	15·37
Remaining in the cakes.	5·4	38·32

The occurrence of free fatty acids in cakes must be ascribed to the action of enzymes on the oil retained in the cakes ; hence those conditions which favour their action, such as a somewhat elevated temperature (between 30° and 40° C.), moisture, etc., will lead to the production of so notable an amount of free fatty acids in stored cakes, that the cakes become unfit for feeding purposes. Nor must the action of light be ignored. This is clearly brought out by an examination of palm kernel cakes made by *Emmerling*.[1] The following changes were ascertained :—

	Free Fatty Acids in 100 parts of Fat		
	I	II	III.
Fresh cakes	14·35	16 14	20 50
Cakes stored two years in the dark	26 44	40 61	
„ „ „ light			86 08

Moulds also lead to the formation of free fatty acids in cakes, as they readily grow on cakes stored in a damp condition. In the case of cakes containing drying oils, such as linseed cake, a slow oxidation of the unsaturated fatty acids takes place, with the production of oxidised acids. Such cakes are known in the trade as cakes that have " heated " in storage or during a voyage.

With regard to poisonous substances (such as saponins, cyanogenetic alkaloids, etc.) occurring in cakes cp. Chap. XIV. under the headings of individual oils and fats, " Linseed Oil," " Rape Seed Oil," " Castor Oil," " Mowrah Shea Butter," " Seed Oil." It has been shown by *Withers and Ray*[2] that the toxicity of cotton seed meal is not caused by pyrophosphoric acid.

Attention should also be directed to the recent practice of " bleaching " (" brightening ") of meal by means of soda and hypochlorites.

(3) *Extraction of Oils and Fats by Means of Volatile Solvents*

The cakes obtained in the foregoing process still contain considerable proportions of oil, usually 10 per cent, and in the case of undecorticated cotton seed cake 4-5 per cent. If it be desired to obtain larger quantities of oils and fats than can be produced economically by expression, processes having for their object the extraction of the seeds by means of volatile solvents must be resorted to.

The solvents employed on a large scale were up to recently almost exclusively carbon bisulphide and petroleum ether. Both solvents suffer from the disadvantage of being readily inflammable.

Extraction of seeds by volatile solvents was first introduced in 1843, by *Jesse Fisher* of Birmingham, who manufactured **carbon bisulphide** on a commercial scale. *Fisher* does not appear to have patented this process. Thirteen years later *E. Deiss*[3] of Brunswick patented the extraction of seeds by means of carbon bisulphide, and added " chloroform, ether, essences, benzine, and benzole " to the list of solvents.

[1] *Landw. Versuchsst.*, 1898, 56.   [2] *Journ. Biol. Chem.*, 1913, 53.
[3] English patent 390, 1856.

For several years afterwards this process made little advance, for the colour of the oils produced was high, and the taste was sharp. The extracted oil retained sulphur, which showed itself disagreeably in the smell of the soaps made from it and in the blackening of substances with which it was used. The meal left by the process was so tainted with carbon bisulphide, that it was absolutely impossible to use the 'extracted meal as cattle food. With the improvement in the manufacture of carbon bisulphide [1] these drawbacks have been surmounted to a great extent, and the employment of carbon bisulphide has specially gained much extension in the extraction of expressed olive marc in the South of France, Italy, Spain, and Tunis. But even at present traces of carbon bisulphide are retained by the extracted mass, so that it is impossible to feed cattle with it. Carbon bisulphide is comparatively cheap; cheaper than the commercial benzine used for extracting fat. Being heavier than water, it offers certain advantages in the storage, as the vapours can be readily prevented from coming in contact with an open flame. Owing to the physiological effect this solvent has on the workmen, and in consequence of the chemical action of impure carbon bisulphide on iron, which has frequently led to conflagration, the employment of carbon bisulphide must remain restricted.

Petroleum ether was first introduced by *Richardson, Lundy, and Irvine,* who obtained in 1863 a patent [2] for extracting oil from crushed seeds or from refuse cake by the solvent action of volatile hydrocarbons from " petroleum, earth oils, asphaltum oil, coal oil, or shale oil, such hydrocarbons being required to be volatile under 212° F." The large quantities of low-boiling hydrocarbons - naphtha - obtained from petroleum at moderate cost, as also improvements in the apparatus originally employed, have brought this solvent in the forefront when extracting processes are considered.

The commercial variety of petroleum distillate for this purpose is usually a petroleum naphtha, boiling between 110° and 120° C.,[3] and having the specific gravity of 0 720 to 0·750. As the boiling point lies above that of water, it is possible to extract, *e g.,* moist bones (for which up to recently petroleum benzine was employed exclusively), the vapours of the boiling naphtha carrying the water vapours with them. Notwithstanding the greater fire risks, naphtha is preferable to carbon bisulphide, for the reasons given already, and for the further reason that it extracts smaller quantities of resinous and gummy matters from the oil seeds, and takes up less colouring matter than does carbon bisulphide. Hence petroleum ether is used exclusively in the extraction of (linseed)

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[1] For the manufacture of carbon bisulphide by means of an electric furnace cp. E. R. Taylor, *Moniteur scientifique,* 1909, 265.

[2] English patent 2315.

[3] Trotman (*Journ. Soc. Chem. Ind.,* 1906, 1202) demands that "benzine" for "degreasing" should distil at 90° to 100° C., and should yield small amounts only below or above these limits. It appears to the author that this specification should only apply to petroleum ether for special purposes, such as degreasing leather. For the extraction of bone fat petroleum ether (of the boiling points given in the text) is mostly used, although it would certainly be advantageous to avoid as much as possible hydrocarbons boiling above 110° C., as their removal is both difficult and expensive.

rape seed and castor seed. By the addition of formaldehyde to seed before extraction with petroleum ether the cake is rendered suitable for cattle food.[1] This must be accepted with reserve.

Ether has found no practical application, as it is far too volatile, and hence far too dangerous. Moreover its cost is too high. **Chloro-form,** as also benzol and acetone, are far too expensive, besides offering other drawbacks which prevent their application on a practical scale.

During recent years efforts have been made to introduce **carbon tetrachloride** on a large scale. This solvent has a lower boiling point than the usually employed petroleum ether, and shares with carbon bisulphide the advantage of being heavier than water. Its chief advantage, however, is that it is non-inflammable, and from this point of view it might be considered an ideal solvent. As further advantages are claimed :—Its low specific heat, its low latent heat of evaporation, and its low boiling point as compared with naphtha. But these slight advantages are not a sufficient set-off against the high price of carbon tetrachloride, which is still too high notwithstanding considerable reductions that have been made during the last few years. For it must be borne in mind that in the extracting process by means of the solvents the *volume* of the solvent and not its weight must be considered. The specific gravity of carbon tetrachloride being 1·632, as against about 0·750 of petroleum naphtha, it follows that for the same volume of solvent more than twice the weight of carbon tetrachloride must be employed. Since the loss of solvent may be taken as amounting in each case to about 1 per cent of the weight employed, and since carbon tetrachloride costs about two to three times as much as petroleum ether, it follows that the actual loss, expressed in money value, must be much greater than in the case of petroleum ether. In view of the many conflicting statements as regards the cost of the carbon tetra-chloride process the following calculation may be found useful (see table, p. 23) :—

1000 kilogs. of petroleum ether require for heating from the ordinary
    temperature, say 15° C. to the mean boiling point, viz. 115° C.,   Calories.
    $1000 \times 0.5 \ (115 \text{-} 15)$ . . . . = 50,000
To vaporise 1000 kilogs. are required 1000×80 . . . = 80,000
                                                      130,000

1000 kilogs. of naphtha occupy a volume of 1333·33 ltr. ; hence 1000
    ltr. of petroleum ether require for vaporisation . . . 97,500

To condense the vapours from 1000 ltr.—on the assumption that the cooling water enters the condenser at the temperature of 15° C. and leaves it with a temperature of 60° C., so that 1 ltr. of cooling water would absorb 45 calories,—there would be required $\frac{97500}{45} = 2167$ ltr. of cooling water.

The same calculation carried out for carbon tetrachloride, using the constants given in the table below, shows that there are required,

[1] Harburger Ölwerke Brinckman and Mergell, German patent application H, 57,783, 1912.

for vaporising 1000 ltr. of carbon tetrachloride, 97,151 calories, and 2159 ltr. of cooling water for condensing the vapours.   The difference in favour of carbon tetrachloride is far too small (even if lower insurance premiums be taken into account) to counterbalance the difference in the cost of the amounts of solvents lost.   As a further drawback must be reckoned the fact that carbon tetrachloride attacks iron and copper very severely, especially in presence of moisture, so that suitable extraction apparatus must be lead-lined or tinned.   In the author's opinion the carbon tetrachloride installations in use, including those made of " homogeneously lead-lined " metal, have not been worked long enough to demonstrate such durability as must be demanded of proper plant, for it is well known that lead does not satisfactorily withstand the corroding action of hydrochloric acid.   In addition to the drawbacks enumerated, it must not be forgotten that carbon tetrachloride exercises on the workmen a physiological action similar to that of carbon bisulphide, and that its vapours are distinctly danger-ous to life.[1]   Nevertheless, several installations were erected in extract-ing works, notably in Marseilles.   It was contended that the bone fat produced with the aid of carbon tetrachloride was of better quality than that obtained with the aid of petroleum ether.   Samples which the author had occasion to examine bear this out, and the explanation would seem to be given by the fact that the extraction with carbon tetrachloride takes place at a lower temperature than is the case with benzine.   The freshness of the bones employed in the preparation of these samples, and their freedom from foreign substances, such as nails, etc., may, however, have had a greater influence than the nature of the solvent.   According to reliable information given to the author, the employment of carbon tetrachloride has been already abandoned in Marseilles.

The choice would therefore practically be between carbon bisulphide and petroleum ether.   In order to enable the reader to carry out calculations such as have been given above, the following table is appended :—

	Chemical Formula.	Specific Gravity at 0° C. (Water 4°=1.)	Boiling Point. °C.	Specific Heat.	Latent Heat of Evapora-tion. Calories.	Vapour Density.	Vapour Tension at 15° C. Milli-metres.
Carbon bi-sulphide	CS_2	1·292	46·0	0·157	79·9	2·63	250
Petroleum ether	...	0·750 (at 15° C)	110-120	0·5	80		
Carbon tetra-chloride	CCl_4	1·632[2]	76·5	0·21	46·4	5·3	67·1

[1] For the examination of carbon tetrachloride cp. L. G. Radcliffe, *Journ. Soc. Chem. Ind.*, 1909, 229.

[2] W. Herz and W. Rathmann, *Chem. Zeit.*, 1912, 1417, express the variation of the specific gravity with the temperature by the following formula :—$d = 1·6309 - 0·0018943\, t$.

In place of carbon tetrachloride, chloro-derivatives of ethane and ethylene [1] have been prepared on a large scale and are now obtainable in the market. The following table enumerates the several solvents, their boiling points, and specific gravities :—

	Specific Gravity.	Specific Heat.	Melting Point	Boiling Point ° C
Dichloro-ethylene,[2] $C_2H_2Cl_2$	1·25			55 [4]
Trichloro-ethylene, C_2HCl_3	1 47 [4]	0 223	− 73	88
Perchloro-ethylene, C_2Cl_4 . (Tetrachloro-ethylene)	1 62 [4]	0 216	19	121
Tetrachloro-ethane, $C_2H_2Cl_4$ [5]	1 60 [4]	0 268	36	147
Pentachloro-ethane,[5] C_2HCl_5	1·70 [4]	0 266	22	159
Hexachloro-ethane,[6] C_2Cl_6				solid

Of these solvents, trichloro-ethylene has been used in a number of works, as it is possible to work with this solvent in iron vessels. It must, however, be pointed out that trichloro-ethylene attacks iron to such an extent that oils and fats obtained with this solvent are deeply coloured by iron compounds. The attack on iron, however, is not so serious that iron apparatus could not be used for " off-coloured " products.

An essential condition for the use of trichloro-ethylene is to reduce the percentage of moisture as much as possible, as in the presence of moisture hydrochloric acid is more readily formed. It should also be pointed out that trichloro-ethylene possesses strong narcotic powers.

Tetrachloro-ethane and pentachloro-ethane are unsuitable solvents

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[1] With regard to proposals for the nomenclature of these chloro-derivatives cp. Margosches, *Chem. Zeit.*, 1913, 509, 519

[2] Cp. German patent 216,070 (*Consortium f. elektrochemische Industrie*).

[3] A preparation boiling from 53-58° C. was resolved by W. Herz and W. Rathmann (*Chem. Zeit.*, 1913, 622) into its two geometrical isomerides, viz. *Cis*-form and *Trans*-form, by repeated fractional distillation The two isomerides had the following constants :—

	$H - C - Cl$			$H - C - Cl$
Cis-form	‖		*Trans*-form	‖
	$H \quad C - Cl$			$Cl - C - H$

	Cis-form	*Trans*-form
Specific gravity .	at 15 /4° 1·2650	at 35°/4° 1,2321
,, ,,	at 25 /4° 1·2189	at 45°/4° 1,2153
Boiling point at 763 mm. .	48·8° C.	59·8° C.

[4] W. Herz and W Rathmann (*Chem Zeit.*, 1912, 1417) express the variations of the specific gravity with the temperature in the case of trichlorethylene, tetrachlorethylene, tetrachloro-ethane, and pentachloro-ethane respectively by the following formulæ :— $d = 1,49486 - 0·001641 \ t$; $d = 1,61861 - 0·0016246 \ t$; $d = 1,6257 - 0·0015073 \ t$; $d = 1,7071 - 0 0014492 \ t$. Cp. also *Chem. Zeit.*, 1913, 621.

[5] Cp. German patent 185,374.

[6] English patent 1105, 1912.

for fat extraction, because they easily give off hydrochloric acid in contact with metals. Although the addition of oil of turpentine, which absorbs hydrochloric acid, is said to obviate the destructive effect on iron, the suitability of these solvents on a large scale must still be considered an open question, quite apart from the feature that their high boiling points would render their employment uneconomical.

The relative toxicity of some of the chloro-hydrocarbons is given by *K. B. Lehmann*,[1] the toxicity of carbon tetrachloride being taken as unity as follows :— $CCl_4 = 1$, $C_2Cl_4 = 1.6$, $C_2HCl_3 = 1.7$, $C_2H_2Cl_2 = 1.7$, $CHCl_3 = 2.2$, $C_2HCl_5 = 6.2$.

Liquid sulphurous acid has been claimed as a solvent by *W. Grillo and N. Schroeder*,[2] but it has not found application in the practice of oil and fat extraction. It would seem that liquid sulphurous acid is more suitable for the purification of mineral oils, as applied in *Edeleanu's* process.[3]

Liquid carbonic acid has been claimed as a fat solvent by *A. Sachs*,[4] but for obvious reasons this has not been found suitable.

With regard to *acetone* and its higher homologues, and to toluene, cp. Vol. III. Chap. XVI.

The type of apparatus employed on a large scale depends on the temperature at which the extraction is carried out. If the extraction is effected in the cold (a procedure which must be considered preferable as regards fire risk in the case of inflammable solvents), the seed is placed in a series of closed vessels through which the solvent percolates on the countercurrent system. The battery of vessels is so arranged that any one vessel can be made the last of the series, ready to discharge the extracted meal, and to be refilled with fresh meal, so that, with the exception of the time required for discharging and recharging, the process is a practically continuous one. The solution of extracted oil or fat in the solvent is then transferred to a steam-heated still, where the solvent is driven off, and recovered by condensing the vapours in a cooling coil, to be used again and again. The traces of volatile solvents retained by the oil or fat
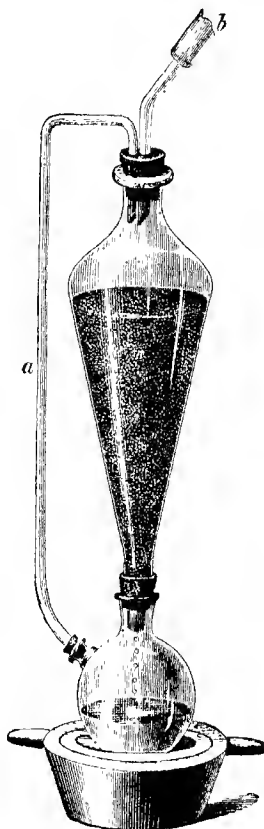
Fig. 7

[1] *Chem. Zeit. Rep.*, 1911, 449.   [2] German patent 5360, 1889.
[3] German patent 216,459.   [4] German patent 163,057, 1904.

are driven off by a current of open steam, which is blown through the oil or fat in the warm state.

The extracting processes in the hot are carried out in apparatus the principle of which is illustrated by Fig. 7. (It should be noted that the condenser is not shown.)

More elaborate forms of apparatus employed on a large scale are designed on the principle involved in the *Soxhlet* extractor. The extraction thus takes place uninterruptedly, with a limited amount of solvent charged once for all into the apparatus. When the seed is deemed completely exhausted, the vessel containing the seed is disconnected by closing taps between the oil-containing vessel and the condenser, so that the volatile solvent can be immediately distilled off and condensed, whilst the meal is freed from the last traces of volatile solvent by open steam, and the seed-containing vessel is emptied and recharged with fresh seed. More compact still are extractors illustrated by that form of laboratory apparatus in which the meal-containing vessel is placed inside the flask charged with the solvent. Thus in some form of extractors a basket containing the crushed seed is placed on a support at some height above the bottom of the vessel; in other forms the seed is placed in trays arranged one above the other. The vessel is then charged with the solvent, so that, on heating, the vapours of the solvent pass through and around the seed, whilst that portion which leaves the vessel in the form of vapour is condensed in a separate condenser, from which the liquefied solvent falls back again to percolate the seed. Finally, when the meal is exhausted, the solvent is driven off with the aid of steam (if permissible), condensed, and collected in a separate vessel.

Frequent attempts have been made to introduce a really continuous process of extraction. On the principle of the counter-current system, the mass to be extracted is moved continually in a series of tubes or vessels through the solvent, so that at the one end of the apparatus the solvent charged with fat is run into the distilling apparatus, whereas at the other end of the battery the extracted meal is discharged into a vessel to be freed from the last traces of adhering solvent. Apparatus of this kind have been patented by *Stevenson*,[1] *E. Bataille*,[2] *G. Mitchell*,[3] *J. E. Mills and H. B. Battle*[4] (in the name of P. M. Justice), *J. Eisenberger*,[5] *E. Evans*,[6] and many others. But, hitherto, none of these apparatus have met with extended use.

Since apparatus of the type described here are illustrated in the catalogues and advertisements of engineering firms, no useful purpose can be served by reproducing them in this work. Nor does it appear necessary to enumerate the very large number of patents which have been taken out during the last twenty-four years. For fully illustrated abstracts of these patents the reader must be referred to the volumes of the *Journal of the Society of Chemical Industry.*

Volatile solvents are used in practice for the extraction of seeds

[1] English patent 28,310, 1902.   [2] French patent 319,204.
[3] German patent 119,134.   [4] English patent 1550, 1909.
[5] German patent 232,370.   [6] English patent 24,111, 1910.

such as soya beans, rape seed, castor seed, etc. They are also employed
for extracting oil from damaged seed (sesamé) which would not yield
edible oil, and from damaged cakes and generally from cakes which are
unfit for cattle food (olive pulp, etc.). Considerably quantities of cocoa
nut oil and palm kernel oil are prepared by extraction, where the oil is
more valuable than the meal.

The seed for treatment with volatile solvents is prepared in a similar
manner as for pressing, except that the seed is not reduced to a fine
meal, which would prevent the free percolation of the solvent through
the mass. Since extracted oil can never be used for edible purposes
(notwithstanding frequent statements by interested parties), the pre-
liminary cleaning of the seed is not carried out as carefully as must be
done in the case of seeds destined for the manufacture of edible oils and
fats ; nor is the preliminary warming of the seed necessary, as the
moisture contained in the seed does not offer a serious obstacle to
thorough extraction. In the case of olive pulp, however, the removal
of the bulk of water (by drying) is imperative.

The removal of the solvent from the extracted seed offers difficulties,
as the meal very tenaciously retains the solvent. If open steam be
passed into the mass, to drive off the last traces of the solvent, the meal
suffers loss in feeding value—provided such meal can be used as cattle
food (see below). It is therefore preferable to dry the meal in special
apparatus, similar to those used in breweries for breaking up and
discharging the refuse, the seed being dried in shallow layers while it is
being continually turned over by a mechanically actuated raking fork.

In order to avoid drying, *Bergman and Berliner*[1] suggest
displacement of the solvent[2] by washing the extracted mass with
acidulated water, or with dilute salt solutions. Whereas this process
might be useful for substances like leather, etc., it is entirely unsuit-
able for meal from oleaginous seeds. In a later patent *Berliner*[3]
suggests heating the oil- or fat-containing material with the same oil
or fat until the water is driven off, as a preparatory operation to the
extraction with volatile solvents.

The extensive use of the extraction process in the treatment of olive
residues and bones has been referred to above. Notable efforts have
been made recently to extend the extracting process to waste products,
such as residues from the preparation of whale oil, seal oil, and fish oil,
also to the extraction of tanned leather, and of all kinds of fat-containing
refuse, such as offal, garbage, greasy rags (cp. Vol. III. Chap. XVI.),
and to the recovery of fat from fuller's earth, used in filtering, etc.

The fact that it is not necessary to dry the substances previous
to their extraction with petroleum ether has been made use of by several
patentees. Thus, *Kaleczok*[4] first suggested the treatment of bones,
without previously drying them, with benzine vapours to extract the
fat, the condensed vapours of benzine and water being separated in a
special vessel. Whereas in this case only small quantities of water are

[1] German patents 157,406 ; 157,407 ; 161,648.
[2] French patent 335,964.
[3] German patent 197,725 ; cp. also Zipser, English patent 12,321, 1912.
    German patent 81,560.

present, the extraction of substances containing considerable amounts of water (such as fruits) with benzine, chloroform, carbon tetrachloride, carbon bisulphide, acetone, and ether is claimed by *Nass-Extraction*, G.m.b.H.[1] The patentees distinctly exclude petroleum ether as offering serious drawbacks to this treatment.

With regard to the merits and demerits of the last two kinds of processes described—expression and extraction with the aid of solvents—the adoption of either will largely depend on local factors and on the purpose for which the resulting products are intended.

It is obvious that extraction processes cannot be employed for the preparation of edible oils and fats, for however carefully the last traces of solvents may be removed, there is left sufficient to impart to the oil or fat a nauseous taste, rendering it entirely unfit for consumption.

Extracted oils and fats can, therefore, only be used for technical purposes.

Extracted meal should also be considered unfit for cattle feeding, notwithstanding the many statements of interested parties, viz. : that the meal is fit for this purpose, and possesses even a greater value than expressed cakes on account of its higher proportion of albuminoids and carbohydrates when contrasted with press cakes. The oil or fat in an expressed cake has undoubtedly a certain value from a stock-raising point of view, whilst extracted meal to which is added so much oil or fat as to equal the proportion contained in the pressed cakes has not the same nourishing value. This holds good even if we leave out of account the contamination of the meal with the non-removable portion of the volatile solvent. In Germany extracted meal, especially rape meal from good Indian seed and palm kernel meal, is stated to be largely used as food for cattle, in admixture with press cakes (manufacture of compound cakes). But against this must be set—and rightly set—the rule of the Deutsche Landwirtschaft Gesellschaft, not to buy any extracted meal which is looked upon as an adulterant if admixed with press-cake meal.[2] It is stated that some extracted meal is put into cakes also in this country, but this practice must be condemned, and the bulk of the extracted meal finds its proper use in manuring the land.

Wherever the cake is the main product, the process of expression will commend itself as the more advantageous one. With regard to those fruits and seeds, however, the fatty material of which forms the main product, as in the case of palm kernel oil and cocoa nut oil, the economical factor militates to a much smaller degree against the extracting process, especially when it is possible to dispose of the extracted meal for feeding purposes. It may, however, be added that whilst cattle will take cakes containing extracted palm kernel oil, they will not eat extracted cocoa nut cake.

In special cases, notably in the manufacture of olive oils (cp. Chap.

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[1] German patent 179,449, 1902.
[2] Under the name "Cleveland meal," solvent-extracted linseed meal is imported from the United States. During the last few years, extracted soya bean meal has been offered in the market as cattle food.

XIV, " Olive Oil "), a combination of the two processes commends itself. The combined method consists in expressing most of the oil for edible purposes, etc., and then extracting the partially expressed material with volatile solvents, in order to recover the oil left in the press cakes. This combined process is known on the Continent under the name " mixed process " (*huilerie mixte*).

Whilst the process of expression is free from danger, the process of extraction involves risks of fire if inflammable solvents are used. But even with non-inflammable solvents there is a risk of explosion through carelessness on the part of the operator. As explosions have actually occurred in practice through some such cause, a warning note may not be superfluous.

The entrance of air into the vessels used for extracting volatile solvents must also be guarded against, as herein lies another source for explosion.

A contrivance for introducing the seed in the absence of air has been patented by the Maschinenbau-Gesellschaft Martini & Huneke G.m.b.H.[1]

If, in the process of expression, the cakes are finally reduced to meal, proper precautions must be taken to remove the dust efficiently, as the meal dust forms with air a dangerous mixture which can be brought to an explosion, as by a spark from an electric motor, etc.[2]

Greater still is the danger attending the comminution of extracted seed-meal.

Commercial Preparation of Waxes

The most important waxes, from a commercial point of view, are the *liquid* waxes sperm oil and Arctic sperm oil. These are prepared on a large scale in the same manner as the animal oils (Chap. XIV.). In the case of sperm oil from the head cavities, the solid wax, spermaceti, is recovered by processes described below under " demargarinating." With regard to the *solid* waxes, frequent attempts have been made to obtain wool grease, the raw material for the manufacture of wool wax (lanoline), from raw wool by extracting with volatile solvents. For this purpose methods described above, under process 3, have been employed, and the solvents actually used were carbon bisulphide and petroleum ether. Recently also carbon tetrachloride has been recommended, but it does not appear to have been used on a large scale. As the wool fibre suffers under the treatment with solvents, the extracting process is used to a very limited extent only. (Cp. Vol. III. Chap. XVI. " Wool Grease.") Most of the wool grease is obtained by scouring the wool with soap or solutions of alkaline carbonates or both. This process may therefore be likened to the first process described under the heading, " Commercial Preparation of Oils and Fats."

Although beeswax forms an important article of commerce, the preparation of the crude wax must be considered a kind of home industry

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[1] German patent 232,614, 1910.
[2] Report by H.M. Inspector of Factories. Cd. 6223.

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of water (such as fruits) with benzine, chloroform, carbon tetrachloride,
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[2] Under the name "Cleveland meal," solvent-extracted linseed meal is imported
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the mucilaginous matter being much more insoluble at temperatures below zero than at the ordinary temperature. The application of artificial cooling for this purpose has been patented by *Niegemann*.[1] Cp. also *T. Buchanan's* process [2] for rapidly heating and rapidly cooling linseed oil.

This method can obviously only be applied to those oils which remain liquid at temperatures below zero (Chap. XIV. " Drying Oils "). Olive oil dissolves a small quantity of water at 20° C. which will separate at 15° C. and make the oil turbid. In other cases the mucilaginous substances are coagulated at temperatures near the boiling point of water and thus settle out more readily. Therefore, washing the oils and fats with boiling water usually leads to a considerable improvement in quality. Thus medicinal castor oil is refined by treatment with steam alone (see Chap. XIV. " Castor Oil ").

In modern establishments the process of clarifying is much shortened by filtering the oils and fats through a filter press (or other kind of filter) at a suitable temperature, or brightening them by blowing with air.[3] In many cases these or similar methods suffice for the production of commercial oils and fats.

Free fatty acids, if present in the crude oils and fats, remain, of course, dissolved in the neutral glycerides. It is therefore evident that oils obtained by such simple methods of purification can only be used in those industries where the presence of free fatty acids offers no serious objection, such as in the candle-making and soap-making industries. In other industries exception must be taken to the presence of free fatty acids. Thus tallow and olive oil containing a high proportion of free fatty acids are unfit for lubricating purposes ; and rape oil containing a high percentage of free fatty acids is unsuitable as a burning oil. In such cases the free fatty acids must be removed by treatment with alkalies or alkaline earths.

The highest grade of purity is demanded of products intended for *edible purposes*. In order to attain this object not only must the raw material (seed, fruit, animal tissue) be carefully selected, and worked up in as fresh a state as possible, but the process of rendering must be carried out with especial care. It has been shown above (Vol. I. Chap. I.) that contact of oils and fats with the organic matter from which they have been obtained (marc of fruit or animal tissues or other nitrogenous substances, such as casein) leads to accelerated formation of free fatty acids, which in their turn seem to dissolve foreign matters. Therefore not only rapidity in the treatment of fresh material but also the greatest cleanliness is required in the preparation of *edible oils and fats*. Exclusion of air so as to prevent deterioration through oxidation is of the greatest importance in the manufacture of readily oxidisable oils such as cod liver oil. But even more resistant oils, such as cotton seed oil, lard oil, etc., intended for edible purposes, should not be exposed to the air in thin layers at elevated temperatures.

In order to remove colouring matters, edible oils and fats are filtered.

[1] German patent 163,056.   [2] English patent 10,326, 1905.
[3] Cp. H. Barringer, English patent 22,401, 1909.

Formerly filter paper [1] (see p. 122) and cotton wool [2] were used, and are to some extent still used in small establishments.   In modern works filtration over charcoal or over natural absorbent earths, such as fuller's earth,[3] Florida earth,[4] etc., is resorted to.   Not all kinds of earth are suitable for this purpose.   Different kinds of earth found in different parts of the world differ considerably in their action.   Thus fuller's earth mined in England is preferable to Florida earth, which, though extremely suitable for mineral oils, is frequently inoperative if applied to vegetable oils and fats.   It is impossible to state general rules, for here also, as is so frequently the case in the oils and fats industries, the behaviour of each individual oil and fat must be studied specially as to the most suitable condition of the powdered earth, the best temperature, and the length of treatment, all of which conditions exercise a considerable influence on the success of the bleaching (refining) processes.[5]

With the exception of alkalies or alkaline earths for the removal of small quantities of free fatty acids (and in the case of edible cotton seed oil for the simultaneous removal of the colouring matter), which may be present in the crude oils and fats, no chemicals must be used in the purifying of **edible oils and fats,** and even this mild treatment with chemicals is avoided by some patentees (see Vol. III. Chap. XV. " Vegetable Butter ").   Notwithstanding the large number of patents which claim effective purification by means of chemicals, no chemically treated oil or fat can be looked upon as a product fit for human consumption.   Methods for the preparation of edible oils and fats, which will be described in Vol. III. Chap. XV., embrace, therefore, exclusively (if we except the treatment with alkalies or alkaline earths) physical methods—such as washing with hot water, filtering over animal char or fuller's earth,[6] etc.   Where required, it is preceded by a process of deodorisation (as in the case of edible cocoa nut oil) which consists in the purification by means of steam.   (For further information, see Vol. III. Chap. XV. " Edible Oils and Fats," " Vegetable Butter.")

The **waxes** being unfit for edible purposes, no such elaborate process of refining [3] is required as in the case of edible oils and fats.

[1] A special filter paper for filtering oils in works is supplied by C. Schleicher and Schull, Duren.

[2] Animal wool as a filtering medium is patented by Soc. Française des Matières Filtrantes (G. Trusson et Cie) in French patent 412,677.

[3] For an earth prepared from clayey schist cp. L. G. Hill, French patent 404,915. Aluminium oxide is patented by Richter, and Richter and L. von Orth in English patent 20,650, 1910 ; the same process has been patented for the bleaching of waxes by the same patentees in English patent 20,649, 1910.   Cp. also R. Schilling (German patents 230,251 and 230,252 ; French patents 419,784 and 419,785), who uses activated aluminium oxide obtained from aluminium amalgam.

[4] Cp. also Macherski and Koperski, English patent 22,942, 1905 ; French patent 377,700.

[5] The recovery of oil from once used fuller's earth has formed the subject of many patent specifications, of which only the most recent ones may be referred to, viz. : B. Noltenius, English patent 8245, 1909 ; French patent 401,517 ; Soc. Anon. Huilerie et Savonnerie de Lurian, French patent 409,915 ; English patent 5009, 1910 ; N. Sulzberger, United States patent 968,092 ; H. Hirzel, German patent 230,250.

[6] Kambara earth, *Journ. Ind. Eng. Chem.,* 1912, 891.

Nor do oils and fats destined for **commercial purposes** require such extreme care in refining as do the edible qualities. The removal of the free fatty acids, as also the improvement of the colour, if need be, by filtering over char [1] or fuller's earth, is carried out in a similar manner to that described above with oils and fats intended to serve as burning oils, paint oils, lubricating oils, etc. (see Vol. III. Chap. XV.). Since the taste is not of paramount importance in judging the quality of commercial oils and fats, bleaching by exposure to the *air* and *sunlight* can be resorted to. Methods of this kind are applied to linseed oil for artists' purposes, as also to the bleaching of beeswax (see Chap. XIV. " Beeswax "). Marine animal oils also are thus bleached, but it should be noted that such oils undergo oxidation at the same time, for the soaps obtained from insolated marine animal oils are dark.

Under this head also falls the process of bleaching oils by exposure to the *Cooper Hewitt* mercury lamp. *Genthe* [2] bleaches linseed oils in this manner for purposes of varnish manufacture (cp. p. 59); he also prepares " boiled oil " by exposing raw linseed oil to the ultra-violet light of an " uviol " lamp (cp. Vol. III. " Boiled Oils " and " Oxidised Oils from Drying Oils "). Recently vegetable oils, stated to have been bleached by exposure to ultra-violet rays, have been placed on the market under the name of " Uviol oils " ; no published information as to these oils is available.

Crude oils and fats, as also those beeswaxes which are more or less deeply coloured, require more elaborate processes of refining, and in most cases a treatment with chemicals is resorted to in the first instance.

The greatest possible stress must be laid on the fact that there is no universal method of refining which is applicable to every and any oil, fat, or wax.

In many cases purification by means of sulphuric acid, invented and patented by *Charles Gower* in 1792 (and frequently ascribed to *Thénard*) is still usefully employed, as in the refining of linseed and rape oils. The method consists in treating the oil or fat with a small percentage of more or less concentrated sulphuric acid—according to the nature of the oil or fat. The acid not only takes up water, but acts on the suspended impurities, carbonising them to some extent, thus causing them to coagulate and separate out in the form of a flocculent mass, which falls down and carries with it mechanically other impurities which have not been acted upon.

Another general method, viz. : the purification by means of strong caustic soda, has been recommended by *Louis C. Arthur Barreswil* at the beginning of the last century, his suggestion being to heat the oil or fat and add 2-3 per cent of a concentrated caustic soda solution. In most cases the purification consisted merely in the removal of the free fatty acids present, the caustic soda forming with the free fatty acids a soap which either rises as a scum and lifts up with it impurities, or falls down to the bottom and carries down impurities. As a rule, however,

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[1] Hence F. M. Berberich (German patent 246,957) patents a method of refining with very dilute solutions of alkali.

[2] German patents 195,663, 223,419.

this method is a very precarious one, as emulsions are formed which in many cases altogether prevent the separation of the oil (see Vol. III. Chap. XV.). After the treatment with acid or alkali the oils or fats are washed with water to remove the last traces of chemicals, and are then further treated by the physical methods described above.[1]

The number of chemical processes which have been proposed from time to time for the last 120 years, and which are still being copied and perpetuated from old text-books, is almost legion. So long as the chemical nature of oils and fats was little understood, a secret trade in oil-purifying chemicals flourished. It has not yet died out completely ; nor has the number of patent specifications claiming the most extravagant results decreased considerably. But our present knowledge enables us to remove most of these chemicals into the limbo of useless things. Too much stress cannot be laid on the necessity of regarding the bleaching of each individual oil or fat as a problem *sui generis*, and of recognising that the processes adopted on a manufacturing scale must vary greatly with the nature of each individual oil or fat. In this chapter it is only intended to give a general survey of this subject on the broadest possible outlines. For the processes applied in practice the reader must be referred to the individual oils, fats, and waxes enumerated in Chapter XIV., as also to Vol. III. Chapters XV. and XVI. It must therefore suffice here to glance very briefly at the chemical methods employed on a large scale.

Bleaching by the aid of **chemicals** requires great circumspection, the object of bleaching being merely to remove or destroy foreign substances, which impart an objectionable colour, or other undesirable properties, to an oil or fat. The chief attention of the operator must therefore be directed to treating the raw material in such a manner that the fatty matter itself is not acted upon. For this purpose the amount of chemicals must be limited to the smallest possible quantity, the temperature at which they are allowed to act must be as low as possible, and the time of interaction must be as short as possible.

General methods of bleaching, the applications of which will be described under the headings of those individual oils and fats for which they are most suitable, are : (1) bleaching by means of oxygen ; (2) bleaching by means of chlorine.

The methods of bleaching by oxygen include all those which aim at the bleaching by exposure to the air and to sunlight (see above), and where oxygen or ozone is introduced in the form of a gas, or is evolved by chemicals, and in some cases assisted by the action of light (ultra-violet light, cp. "Linseed Oil," p. 45). Under the head of ozone would also fall those processes where ozone is generated by electrical methods, as in *de Hemptinne's* process (see Chap. XV. "Fish Oil"). Bleaching by means of oxygen gas or ozone is still too uncertain a process to be used widely on a large scale, although it is practised with

[1] Processes for removing free fatty acids by means of alcoholic potash were patented by Urbain and Feige, French patent 361,966 ; by P. H. Klein, French patent 348,010 ; and E. Jaeschke patents in German patent 254,024 a process for removing the fatty acids by treating oils and fats with an alkaline solution of sugar, containing the requisite amount of alkali for complete saturation of the free fatty acids.

success in some special instances.   Bleaching by oxygen *in statu nascendi* is chiefly effected by employing manganese dioxide or potassium bichromate (less frequently permanganate), and sulphuric acid.

The chemical reactions involved are expressed by the following three equations :—

$$(1)\ MnO_2 + SO_4H_2 = SO_4Mn + H_2O + O\ ;$$
$$(2)\ Cr_2O_7K_2 + 5SO_4H_2 = (SO_4)_3Cr_2 + 2SO_4KH + 4H_2O + 3O\ ;$$
$$(3)\ Mn_2O_8K_2 + 4SO_4H_2 = 2SO_4Mn + 2SO_4KH + 3H_2O + 5O.$$
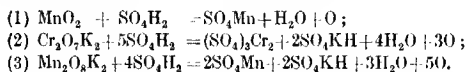
Hydrogen peroxide, sodium peroxide,[1] calcium peroxide, barium peroxide (see Chap. XIV. " Bone Fat "), as also persalts [2] (perborates, persulphates,[3] percarbonates of sodium or potassium), organic peroxides (benzoyl peroxide,[4] acetyl peroxide, acetone peroxide) have been recommended (under fancy names) as effective bleaching agents, but no definite statement can be made as to their usefulness or superiority over the reagents named above.

(2) In the processes of bleaching by means of chlorine, bleaching powder, chloride of lime, or potassium bichromate (less frequently permanganate) and hydrochloric acid are used.   The following three equations represent the chemical reactions involved :—

$$(4)\ Ca(ClO)_2 + 4HCl = CaCl_2 + 2H_2O + 4Cl\ ;$$
$$(5)\ Cr_2O_7K_2 + 14HCl = Cr_2Cl_6 + 2KCl + 7H_2O + 6Cl\ ;$$
$$(6)\ Mn_2O_8K_2 + 16HCl = 2MnCl_2 + 2KCl + 8H_2O + 10Cl.$$
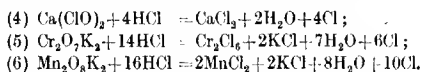
Recently a number of reducing agents, such as sulphites [5] and hydrosulphites,[6] have been placed on the market (under fancy names), and are recommended as effective bleaching agents for oils and fats. To this class belong " formaldehyde-hydrosulphites," " sulphoxylates," [7] and " formaldehyde-sulphoxylate," [8] of sodium, zinc, etc., also " Hyraldité," a stable compound consisting of a combination of sodium hydrosulphite and ammonia.

It may be repeated that no general rule can be laid down as to which process should be employed in each given case, although it may be stated that tallow is best bleached by means of manganese dioxide, and palm oil by means of bichromate and hydrochloric acid.

The object of bleaching is not only to remove colouring matters for the time being, but to remove them so efficiently that the colour,

[1] Cp. L. Vanino, *Das Natriumperoxyd*, Hartleben, Vienna, 1907 ; Foregger and Philipp, *Journ. Soc. Chem. Ind.*, 1906, 298.

[2] Vereinigte Chemische Werke, French patent 377,720 ; 378,515 ; German patent 200,884.

[3] *Idem* , German patent 205,067.

[4] *Idem.*, German patent 214,937.

[5] For laboratory experiments regarding the action of sulphur dioxide upon oils and their fatty acids cp. S. A. Hird and L. L. Lloyd, *Journ. Soc. Chem. Ind.*, 1912, 317.

[6] Cp. K. Jellinek, *Grundzüge der physikalischen Chemie des Hydrosulfits im Vergleich zu analogen Schwefelsauerstoffverbindungen.*   Stuttgart, F. Enke, 1911.

[7] Metz and Clarkson, English patent 11,983, 1906 ; Badische Anilin und Sodafabrik, French patents 431,294, 410,824 ; English patents 16,260, 1909 ; 12,157, 1911 ; 22,453, 1911 ; 3433, 1912 ; German patent, 224,394 ; Chemische Fabrik Gnesheim Electron, English patent 21,359, 1911.

[8] Chem. Fab. von Heyden, German patent 214,043.

or even a dark shade, does not " revert " some time after the fat or oil
has been bleached. Patents claiming to effect this object appear
annually in great numbers, and disappear again when experience has
shown that the colouring matter does " revert," to a larger or smaller
extent, after the material has, e.g., been converted into soap. One
of the simplest and most frequently practised processes, that of
bleaching tallow, does not lead to soaps having as good a colour as
those made from freshly rendered tallow. Therefore, not only must
each kind of oil or fat be considered a special problem, but frequently
different varieties of one and the same oil or fat are apt to cause the
same difficulties as would a new individual.

In conclusion it may again be emphasised that, in the absence of
careful experiments, it is impossible to state which method of bleaching
will be successful in each given case. There is a wide field open for the
application of proper processes for the removal of impurities and colour-
ing matters, without running the risk of attacking the glycerides them-
selves. Even in the case of the more resistant waxes great circum-
spection is required, as is evidenced by the different properties of
beeswaxes bleached by different processes. (See Chap. XIV. " Bees-
wax.")

Demargarinating Oils and Liquid Waxes.   Separation into
" Stearine " and " Oleine "

Solid glycerides and solid waxes separate out from some oils and
liquid waxes on standing. The deposited glycerides are commercially
known under the name of " stearine," or " margarine " (" cotton seed
stearine," " margarine d'arachide "). In some cases this deposit is
objectionable, especially so in the case of edible oils intended for table
use. An important part in the sequence of the refining operations of
such oils is therefore played by processes aiming at the removal of the
solid portions. The simplest demargarinating process, which is still
being used to some extent, consists in storing the oils in capacious
vessels in a cool place, when the solid glycerides or waxes, as the case
may be, separate out as a deposit, so that the clear limpid oils can be
drawn off from the upper parts of the vessels.

If the solid glycerides separate out in a crystalline form, this slow
and cumbersome process can be shortened by cooling the oils artificially.
A definite temperature must be carefully maintained for each individual
oil. The liquid portion is then filtered off ; when the whole has solidified
to a magma, the oil is pressed in a hydraulic press. In other cases
where the solid glycerides separate out in a gelatinous form, and filtering
or pressing is unavailable (see Vol. II. Chap. XIV. " Arachis Oil "), the
old process of sedimentation must be resorted to. (Cp. also Vol. II.
Chap. XIV. " Cod Liver Oil," " Lard Oil," " Sperm Oil and Sperma-
ceti " ; Vol. III. " Edible Cotton Seed Oil.")

The limpid oils which remain proof against cold are termed " winter
oils." Most of the olive oils are non-congealing oils ; some Tunisian

and Algerian olive oils deposit, however, so much stearine that they must be " demargarinated " before being placed on the market. For the latter purpose, centrifugals [1] have been proposed, but nothing definite can be stated as to their success. It appears to the author rather doubtful whether proper demargarination can thus be effected.

In a wider sense, the term " demargarinating " includes also those processes in which fats which are solid at the ordinary temperature are resolved into two portions of different consistence, generally termed " stearine " and " oleine." As examples may be given the preparation of oleomargarine and tallow oil from tallow, of lard oil from lard (see Vol. III. Chap. XV.), and the separation of oleic acid from stearic acid.

Preserving Oils and Fats

It has been pointed out in the first chapter that oils and fats, if carefully protected from access of light, air, and moisture, retain their state of neutrality indefinitely, and in confirmation the fact was adduced that fats buried with the mummies in Egyptian tombs had remained neutral for several thousand years.

In practice it is, of course, impossible rigidly to exclude contact with air during handling, and it is a matter of daily experience, most noticeable in the case of edible oils and fats, that in course of time, sooner or later, according to the conditions observed in keeping, they turn rancid.

The cause of rancidity has been traced, in the first instance, to initial hydrolysis (see Vol. I. Chap. I.), which is accelerated in the case of unrefined oils and fats by the presence of enzymes. In the preparation of the majority of commercially prepared oils and fats, the enzymes may be considered as having been destroyed, owing to the elevated temperature employed in the refining operations. Where, however, large quantities are prepared merely by rendering at low temperatures (premier jus, lard), the temperature may not be sufficiently high throughout the whole mass to destroy the enzymes completely, so that there may remain intact a quantity of enzymes sufficient to cause hydrolysis and subsequently rancidity.

Where the possibility of accelerated hydrolysis due to the presence of enzymes is excluded, a small amount of moisture is sufficient, under favourable conditions (the most important of which is a somewhat high temperature), to cause hydrolysis and rancidity which follows in its wake. It is therefore obvious that it is not only necessary to employ the greatest care in refining, but that it is essential for the preservation of the refined product to exclude as far as possible the presence of moisture. Since, however, even properly filtered fats retain water up to one-half per cent, without revealing its presence by a turbid appearance, oils and fats should be stored at as low a temperature as possible.

In the case of edible oils and fats (which demand the greatest care

[1] E. Bertainchand, *Démargarination des huiles de la région de Sfax.* Tunis, 1903.

and most scrupulous cleanliness both as regards preparation and packing of the finished article, etc.), cold storage is resorted to as the most effective and most reliable method of preservation.

The low temperature not only arrests the natural process of hydrolysis but inhibits also the injurious action of air on free fatty acids that may be present. No chemical need be used as a preservative for *pure* oils and fats. In fact, they in their turn are largely used as preservatives for perishable food-stuffs, since oils and fats do not afford a substratum for the growth of micro-organisms (cp. Vol. I. Chap. I.[1]). If, however, suitable nutriment is provided, together with the glycerides, as happens in the case of *butter* and *margarine*, then in addition to all those causes which favour the setting in of rancidity, the micro-organisms exert their deleterious influence on the albuminoids contained in butter and margarine. In these cases preservatives are not only used largely but are necessary.[2] The most commonly used and entirely unobjectionable preservative is salt. The quantity of salt usually added to butter is sufficient to preserve it for some little time, which for practical purposes is sufficiently long. But in consequence of the demand for unsalted butter, and further, owing to the development of the enormous shipping trade in butter from oversea countries—necessitated by the insufficiency of supply from local sources—the employment of other, more powerfully acting preservatives has become almost universal, and has therefore been permitted by law. Foremost amongst these is boric acid. Of course, preservatives of a distinctly poisonous nature, such as sodium fluoride and formaldehyde, are forbidden. With regard to other preservatives, see Chap. XIV. " Butter."

Of minor importance is the preservation of fats by means of such substances as cinnamic acid[3] and gum benzoin. The latter is chiefly used in the pharmaceutical practice to preserve lard.

Denaturing Oils and Fats

In those countries where differential custom duties are levied on oils and fats according as to whether they are used for edible purposes or commercial purposes, oils and fats serving for the latter purposes must be " denatured." Thus in Australia edible rape oil must be " denatured " with blown rape oil and birch tar oil. In Germany edible cotton seed oil must be " denatured " with rosemary oil.

" Denatured " oils and fats after having passed the custom-house cannot be considered as adulterated. In their examination, due regard must be had to the presence of those denaturing agents which the law prescribes.

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[1] For a conserving mixture consisting chiefly of oils and fats cp. S. Fenger, English patent 13,382, 1907 ; cp. also X. Rocques.

[2] In some countries butter and margarine are preserved by melting them, so that separation into two layers takes place, and the supernatent milk fat or mixture of fats can be drawn off (see " Ghi Butter," Chap. XIV. ; " Butter " and "Schmeltzmargarine," Vol. III. Chap. XV. "Margarine "). This method is, of course, tantamount to a process of removing albuminoids and carbohydrates.

[3] Cp. French patent 371.071. P. A. Sparre.

In this chapter only those oils, fats, and waxes have been considered which are obtained from sound raw material as the main product, or at least as a very important by-product, and thus form the staple products of the oil and fat industries. Oils, fats, and waxes obtained as *waste products* (by-products), and the mode of working up these materials will be treated of in a separate chapter (Vol. III. Chap. XVI., and also under "Bone Fat," Vol. III. Chap. XV.).

CHAPTER XIV

TECHNOLOGY OF THE NATURAL OILS, FATS, AND WAXES ; METHODS OF PREPARING, REFINING, EXAMINING THEM, AND DETECTING ADULTERATIONS

In this chapter the individual natural oils, fats, and waxes are arranged according to the classification outlined in Chapter I. In the first instance, the source and the mode of preparation will be given, and the methods of refining will be considered, wherever this is carried out on a large scale. Next, the chemical composition will be discussed, as far as it is known. I append in each case tables of the physical and chemical characteristics, as recorded by different observers, and I further add the variations—within narrow limits—of these characteristics, wherever these variations are due to difference of source, climate, soil, mode of preparation, race or breed of animal, mode of feeding, and, finally, age of the sample. Thus this chapter furnishes in a handy form that information which is obtained by applying the methods described in Vol. I. Chaps. V.-XI.

It is hoped that by first scanning the tables the analyst will have placed before him a ready means of identifying any unknown oil or fat which he may have to examine. In each case a discussion of those factors will follow which influence the chemical composition. Next, those adulterants will be considered that are most likely to be met with. Methods of testing for adulteration and determining its amount will also be fully described. It should be mentioned that I have examined in the course of many years most of the products described below ; especially those that are of great commercial importance, although I did not consider it necessary to record my name in each case amongst the observers. It should, however, be pointed out that the colour reactions to which, in former years, so much importance has been assigned, have been especially examined by me. In the course of these investigations most of the colour tests have been found useless, and have therefore been omitted in this treatise.

The order in which the natural oils, fats, and waxes are enumerated in the subsections is determined by the magnitude of the iodine value. I have frequently ascertained the iodine values merely for the sake of fixing the order which individual oils or fats should follow. I have, however, not considered it advisable slavishly to follow this principle ;

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hence such oils and fats as are undoubtedly related to one another are placed together irrespective of differences in their iodine values.

It should further be pointed out that I have carefully scrutinised the numerical values given in the tables. Older numbers which are obviously wrong, or have been obtained by incorrect methods, have been omitted, and only the most reliable numbers have been tabulated.

The technical uses and applications of the natural oils, fats, and waxes are explained fully, and statistical data have been added whenever ascertainable, the reliability of the sources of the commercial information being considered of supreme importance. The changes which the oils and fats undergo in the oils and fats industries are indicated and references are given to Vol. III., in which manufactured products are considered.

Thus an attempt has been made to furnish in this chapter, in as concise a form as possible, a complete series of monographs of all known natural oils, fats, and waxes.

The French, German, and also Italian names of each individual natural oil, fat, and wax have been added.

A. OILS AND FATS.   GLYCERIDES

I. OILS OR LIQUID FATS

1. VEGETABLE OILS

(1) DRYING OILS

The drying oils are characterised by the property of absorbing oxygen from the atmosphere, and drying to an elastic skin when exposed to the air in a thin layer. It has been pointed out already (Vol. I. Chap. VII.) that the drying power stands in direct proportion to the magnitude of the iodine value, so that the best drying oils are those which absorb the greatest amount of iodine.

Considered chemically, the vegetable drying oils are characterised by glycerides of fatty acids belonging to the linolenic and linolic groups, oleic acid forming only a small proportion of the liquid fatty acids. Hence the drying oils do not give the elaïdin reaction (see Vol. I. Chap. VII.). Glycerides of saturated acids are present in small proportions only.

As regards drying power, the oils enumerated below exhibit a slow gradation, from the best drying oils down to those standing at the end of the class, the properties of which approach more or less those of the semi-drying oils. In the best drying oils, linolenic acid forms a considerable proportion of the liquid fatty acids. The readiest means of ascertaining the amount of the linolenic acids is afforded by the bromide test (see Vol. I. Chap. VIII.).

PERILLA OIL

French—*Huile de perilla.*   German—*Perillaöl, Okumiöl.*
Italian—*Olio di perilla.*

Perilla oil is obtained from the seeds of *Perilla ocimoides*, L. (Japanese : *Yé goma, Yé no-abura*), an annual *labiate* indigenous to the south-east of Asia, *i.e.* China, Japan, and the northern parts of India— where it is cultivated extensively for the sake of its oleaginous seed. The plant cultivated in southern Manchuria [1] is most likely identical ·with *Perilla ocimoides*, L. (*Perilla heteromorpha*, Carr). It is sown in April, blossoms about the end of September, and ripens two weeks later.

[1] A. Hosie, Manchuria, Methuen and Co., 1901.

Perilla arguta, Benth (Japanese: *Sissoo* òr *Jakosju*), and *Perilla nankinensis*, Deene,[1] are indigenous to Japan and China; the former is, cultivated in Japan as an oleaginous plant. *Perilla nankinensis*, Decne, (*Ocimum crispum*, Thunberg), is indigenous in Nankin, but is also largely found in East India.[2] The fatty oil of the two last-named perilla species has not yet been examined.

Up to two or three years ago perilla oil (Japanese: *Yé no-abura*) was practically unknown in Europe; but the exceedingly high price of linseed oil obtaining during these latter years directed attention to perilla oil, which, on account of its high iodine value, was predestined to serve as a substitute of linseed oil. Hence notable quantities of perilla oil were imported into Europe, and attempts were even made to grow the plant in the United States (Ohio). These experiments have been abandoned already in consequence of the unsatisfactory nature of the cakes. Japanese cakes have also been offered on the Continent as "Susza-cakes"; they have a peculiar aromatic [1] smell and taste. *Bredemann* [2] gives the following analysis :—

		Per cent.
Oil	.	8·34
Water	.	9·6
Ash	.	8·70
Sand	.	2·50
Proteins	.	37·65
Crude fibre	.	17·76
Silica	.	0·25

The proportion of oil in the seeds is stated to be 35·8 per cent (*Wijs*); 45 per cent (*Ch. P. Fox* [3]).

This oil has the highest iodine value of any known fatty oil, and simulates linseed oil in taste and smell. Contrary to expectation, its drying power is inferior to that of linseed oil, although it absorbs up to 20·9 (*Wijs* [4]) to 25·9 (*Rosenthal* [5]) per cent of oxygen. The inferiority in drying is due to the curious property of the oil of forming drops when spread on a surface; in recently imported perilla oils the author could not observe this property to such a pronounced degree, although, in some cases, the oil runs together in streaks. By heating to 250° C. the oil becomes much paler, and then behaves like a good drying "boiled oil." No doubt polymerisation takes place on heating.

The mixed fatty acids of perilla oil consist of linolenic, iso-linolenic, linolic, oleic, palmitic, and stearic acids, according to examinations made by *K. Kimura and T. Kametaka* (*Journ. Tokyo Chem. Soc.*, 1906 [6]).

[1] The ethereal oil of *Perilla nankinensis* has been examined recently by F. W. Semmler and B. Zaar, *Berichte*, 1911, 52, 460, 815.
[2] For a description of the seeds, etc., cp. G. Bredemann, "Über Presskuchen der Perillasaat" (*Landw. Versuchsst.*, 1912, 349). Cp. also F. Honcamp, M. Reich, and H. Zimmermann, *Landw. Versuchsst.*, 1912 (78), 321.
[3] *Journ. Ind. Eng. Chem.*, 1912 (4), 229.
[4] *Zeits. f. Unters d. Nahrgs- u. Genussm.*, 1903, 492.
[5] *Farben. Zeit.*, 1912 (17), 739.
[6] Private communication by M. Tsujimoto.

Physical and Chemical Characteristics of Perilla Oil

Specific Gravity. At ° C.	Saponification Value. Mgrms KOH	Iodine Value. Per cent.	Maumene Test. ° C	Refractive Index.	Observer.
(Water 20° = 1) 0·9306	189·6	206·1	.	.	Wijs
15 0·9280	188·6	181·2¹	.	1·48249 at 15° C	Niegemann
15 0·9305	190·6	196·3	124	1·4753 at 40°	Rosenthal

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Fatty Acids +Unsaponifiable. Per cent.	Specific Gravity. At 20°	Melting Point. ° C	Neutralisation Value. Mgrms KOH	Mean Molecular Weight.	Iodine Value. Per cent	Hexa-bromides.² Per cent	Maumene Test. ° C	Refractive Index.	Observer.
		- 5	197·7	284·0	210·6				Wijs
95·87						51·15			Niegemann
	0·9235		199·1		199·9	45·6³	130	1·4662	Rosenthal

¹ This specimen contains 16·2 per cent oxidised acids, hence cannot be considered a normal oil
² Ebner and Muggenthaler found by their method, Vol. I. Chap VIII., 64·0 per cent hexabromides of the melting point 177° C.
³ The melting point is given at 172-174° C. As the same sample is stated to have yielded 54·1 per cent of hexabrominated glycerides, the figure given in the table must be accepted with reserve.

In view of some discrepancies shown in the figures given in the tables of " Physical and Chemical Characteristics," the following determinations, due to *M. Tsujimoto*,[1] will be found useful :—

	Seeds from	Colour of Seed	Specific gravity 15 5° C. (water at 15 5°—1)	Acid Value	Saponification Value.	Iodine Value.	Refractive Index at 15° C
Cold-drawn oils, prepared in the Laboratory	Hokkaido, harvested in 1903	black	0 9342	1·31	193·48	196·45	1 4836
	,, ,,	white	0 9343	0·81	193·35	195·72	1·4837
	,, 1904	black	0 9345	0·98	193 47	197·14	1·4836
	,, ,,	white	0·9342	2 79	193·88	196·75	1·4835
	Aomori ,,	black	0·9346	1·90	192·17	201·82	1·4840
	Tochigi ,,	,,	0·9343	2·83	193·39	202·45	1·4851
	,, ,,	,,	0 9343	1·99	193·20	200·42	1·4841
	,, ,,	,,	0·9343	0·84	193·31	200·56	1·4841
Commercial oils	Tochigi, 1904	black	0·9332	7 62	193 11	193·78	1·4831
	,, ,,	,,	0·9318	6·57	193·48	185·65	1·4822
	,, ,,	,,	0·9344	5 17	193·36	200·46	1·4840
	,, ,,	,,	0·9372	2·69	193·12	190·22	1·4840
	,, ,,	,,	0 9338	2·82	191·67	196·00	1·4835
	,, ,,	,,	0 9325	2·53	189·67	187·48	1·4826

In India, China, Manchuria, and in Japan,[2] the oil is used for edible purposes. In Japan it is used for mixing with the cheapest kinds of lacquer [3] (as much as 30 per cent of oil being used) for the preparation of paper umbrellas, lanterns, and artificial leather. It also finds extensive employment in the manufacture of printers' inks, paints, and varnishes. The statement that perilla oil is also employed in the extraction of the last quantities of Japan wax from the berries by mixing the press residues with 10 per cent of perilla oil is erroneous.[1]

The annual production of perilla oil in Japan is estimated to amount to 350,000 gallons.

LINSEED OIL, FLAX SEED OIL

French—*Huile de lin.* German - *Leinöl, Flachssamenöl.*
Italian —*Olio di lino.*

For tables of characteristics see pp. 51-53.

Linseed oil is obtained from the seeds of the flax plant, *Linum usitatissimum*, L., a native of Central Asia. The principal countries where it is grown in considerable quantities to yield *oil seeds* are Argentina, India, the United States of America, Canada, and Russia. Notable quantities of seed are also produced in Morocco. Attempts are being made to grow linseed in the Transvaal and in Australia.

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[1] Private communication by M. Tsujimoto.
[2] A. Hosie, Manchuria, Methuen and Co., 1901.
[3] J. J. Quin, *British Consular Report from Tokio*, 1882.

In the following tables statistical data with regard to the most important producing countries are given :—

Production of Linseed in the principal Linseed-growing Countries

(Metric tons of 1016 kilograms)

Year.	Argentina.	India.	U S A	Canada.	Russia	Total.
1892	85,000	487,000	260,000	.	234,000	1,066,000
1893	120,000	584,000	236,500		363,400	1,303,900
1894	270,000	625,000	177,000		403,500	1,475,500
1895	250,000	326,000	355,000		566,500	1,497,500
1896	185,000	358,000	402,000		703,970	1,648,970
1897	160,000	220,983	273,000	. .	520,552	1,174,535
1898	260,000	446,668	412,500		563,409	1,682,577
1899	250,000	427,894	437,500		316,570	1,431,964
1900	389,951	295,674	475,000		533,877	1,694,502
1901	365,035	336,136	650,000	6,660	455,444	1,813,275
1902	763,976	342,624	732,122	18,065	542,234	2,399,021
1903	937,601	481,567	682,513	21,100	461,314	2,584,097
1904	740,000	571,832	585,013	13,388	471,846	2,382,079
1905	591,912	347,400	711,944	18,342	421,000	2,090,598
1906	825,764	353,400	626,500	25,588	540,500	2,371,752
1907	1,100,710	425,200	646,275	45,301	550,590	2,768,076
1908	1,048,852	163,200	645,125	79,133	500,339	2,436,649
1909	716,515	297,700	487,817	120,829	558,360	2,181,221
1910	595,000	527,600	317,950	100,974	650,000	2,191,524
1911	572,000	563,600	484,250	196,675	670,000	2,486,525
1912	1,130,000	641,200	701,825	528,505	650,000	3,651,530

Exports of Linseed from the principal Linseed-growing Countries

(In metric tons)

Year.	Exports from					Imports into Great Britain		Imports to Continent and to United States
	Argentine	India	U S.A.	Russia	Total.	Metric Tons	Per cent	
1896	230,000	365,810	77,211	481,071	1,154,092	457,362	40	. .
1897	169,092	177,975	26,784	460,038	833,889	349,020	42	. .
1898	142,442	375,908	55,839	220,270	794,459	301,787	38	. .
1899	230,550	416,276	64,641	182,337	912,804	314,148	35	. .
1900	210,693	257,593	52,148	200,643	721,077	309,108	43	. .
1901	336,509	315,378	72,834	55,377	780,098	282,048	36	. .
1902	332,830	311,159	88,585	93,039	825,613	308,331	37	. .
1903	608,307	417,946	18,640	133,257	1,178,150	385,954	33	592,196
1904	919,056	527,710	180	76,660	1,523,606	505,519	33	1,017,907
1905	662,264	331,541	22,325	94,643	1,110,773	345,412	31	795,361
1906	531,132	221,155	218,436	110,160	1,080,883	286,140	26	794,743
1907	831,887	335,214	122,657	78,553	1,368,511	372,537	27	995,774
1908	1,078,084	162,829	42,400	148,873	1,432,186	382,169	26¾	1,050,017
1909	925,660	236,814	33,314	98,050	1,293,836	303,237	23½	990,599
1910	652,830	350,731	6,430	143,932	1,153,923	236,066	20½	917,857
1911	455,000	524,873	nil	126,817	1,106,690	243,338	22½	858,352
1912	545,566	356,797	53,000	172,061	1,127,424	257,294	23	870,130

The requirements of the United States of America are no longer filled by home-grown linseed; hence linseed is being imported since 1908. The following table gives some details :—

United States of America Imports of Linseed (in tons)

From	1908	1909	1910	1911	1912
Canada			72,007	12,466	143,014
Argentina			110,548	91,634	38,196
India			21,449	66,935	13,649
Belgium			9,075	8,870	460
Other countries			10	933	460
United Kingdom			15,880	6,165	50
	1,118	36,991	228,969	187,003	195,829

These tables may be supplemented by the following table, giving the shipments of linseed to Europe during the years 1900–1912 :—

Shipments of Linseed to Europe

(In quarters [1])

From	India		Argentina		Russia and Black Sea	
To	United Kingdom.	Continent.	United Kingdom.	Continent.	United Kingdom.	Continent.
Year						
1900	636,000	768,000	518,500	616,000	320,000	740,000
1901	758,000	958,000	940,000	844,000	167,000	125,500
1902	661,000	1,031,000	891,500	872,500	210,500	271,500
1903	801,000	1,497,000	1,418,000	1,857,500	282,000	422,000
1904	1,068,000	1,797,000	2,665,500	2,196,000	199,500	207,000
1905	518,000	1,279,000	2,076,500	1,400,500	252,500	247,500
1906	441,000	752,000	1,188,000	1,627,000	243,000	339,000
1907	741,389				182,884	
1908	409,010		967,906		269,068	
1909	540,161		1,205,147		179,377	
1910	774,665		873,617		229,504	
1911	833,107		398,062		183,199	
1912			331,464			

[1] 1 quarter of Indian linseed = 410 lbs.
   1   ,,   Argentine linseed = 416 lbs.
   1   ,,   North American linseed = 424 lbs.
   1   ,,   Russian linseed = 424 lbs.

[TABLE

From	U.S. America		Canada to United Kingdom.	Total.	
To	United Kingdom.	Continent.		United Kingdom.	Continent.
Year.					
1900	68,000	207,500		1,542,500	2,331,500
1901	79,500	310,000		1,964,000	2,237,500
1902	105,500	362,000		1,868,500	2,537,500
1903	24,000	74,500		2,525,000	3,851,000
1904	...	1,000		3,934,000	4,201,000
1905	20,000	98,000		2,867,000	3,025,000
1906	281,000	873,000		2,153,000	3,591,000
1907	64,814		78,277	2,071,534	..
1908	71,488		47,199	2,067,195	
1909	35,298		25,808	1,697,428	
1910	22,643		7,028	1,478,259	
1911	1,217			1,393,874	

Further statistical data are supplied in the following tables :—

Production of Linseed in France and Imports into France

(In metric tons)

Year.	Production	Imports from				
		Russia	India.	Argentina.	Other Countries	Total
1896	13,288	25,709	56,475	42,546	10,436	135,616
1897	13,306	50,422	27,375	56,615	7,571	141,983
1898	9,069	11,008	67,307	30,235	3,115	111,556
1899	8,769	8,915	76,320	38,023	4,298	127,556
1900	12,515	31,484	32,060	33,300	7,976	104,820
1901	15,519	9,966	40,452	44,621	14,071	109,110
1902	11,426	7,330	40,771	39,846	14,360	102,307
1903	13,826	4,009	61,680	83,014	8,422	157,115
1904	15,438	2,434	67,434	90,064	8,701	168,636
1905	14,602	2,758	69,044	75,337	9,553	156,642
1906	16,410	8,233	43,737	73,218	18,809	143,997
1907	...	5,170	90,561	84,990	8,379	189,100
1908	...	4,616	56,645	113,890	11,689	186,845
1909	..	9,864	59,900	91,905	7,776	169,450
1910	...	7,085	65,807	62,387	5,582	140,862
1911	...	10,061	77,187	21,973	9,590	119,117

Imports of Linseed into Germany

(In metric tons)

Year.	Imports from						
	Holland.	Russia.	India.	Argentina.	U.S.A.	Other Countries.	Total.
1896	20,390	169,009	69,833	19,241	2,763	7,864	289,100
1897	25,064	172,709	50,841	7,307	2,464	3,869	262,254
1898	23,389	106,106	99,927	30,328	5,472	4,724	269,946
1899	15,256	101,654	114,275	22,938	8,048	3,848	266,019
1900	14,702	107,523	80,405	41,013	17,966	5,962	267,571
1901	9,800	58,950	66,370	74,590	21,740	5,480	236,930
1902	6,990	49,150	74,670	84,340	25,240	5,570	245,960
1903	2,290	47,000	112,540	151,010	4,940	13,370	331,150
1904	1,860	41,920	139,680	262,940	8,010	8,310	462,720
1905	1,040	49,070	110,300	181,930	3,820	7,320	353,480
1906	3,920	55,056	48,801	195,670	69,767	5,609	378,823
1907	1,525	28,270	47,618	334,170	22,079	7,197	439,859
1908	...	...	...	...	...	...	468,422
1909	...	...	...	...	...	...	436,867
1910	...	...	...	215,073	...	...	320,522
1911	2,319	50,733	75,036	144,117	...	4,138	276,343
1912	3,488	74,754	69,802	173,273	...	8,775	330,092

The area of land on which linseed was grown in the different provinces of India during 1905–1907 and 1909–1910 is stated in the following tables :—

Province.		1909-10.	1905-07	Average of	
				Five Years	Ten Years.
United Provinces	Pure	315,000	210,900	554,800	472,700
	Mixed	633,000	567,000	565,000	500,000
Bengal		671,800	726,500	728,100	626,900
Eastern Bengal .		87,700	103,000	113,000	123,000
Central Provinces and Berar		1,145,200	912,100	729,100	684,900
Bombay		144,200	154,800	298,600	289,900
Hyderabad		664,300	604,500	485,000	421,000
Total	Pure	3,028,200	2,711,800	2,908,600	2,618,400
	Mixed	633,000	567,000	565,000	500,000

Linseed Crop under Cultivation in 1909–1910

						Acres.
Bengal	.	.	.	.	.	585,700
Eastern Bengal	.	.	.	.	.	85,100
Assam .	.	.	.	.	.	11,003
United Provinces (Agra)	.	.	.	.	243,129
United Provinces (Oudh)	.	.	.	.	67,068

Linseed Crop under Cultivation in 1909–1910 (*continued*)

					Acres.
Punjab	.	.	.	.	36,268
North-West Frontier Province	.	.	.	16
Upper Burma	.	.	.	.	139,013
Lower Burma	.	.	.	.	1,685
Central Provinces	.	.	.	.	875,199
Berar	.	.	.	.	51,035
Ajmer-Merwara	.	.	.	.	718
Coorg	.	.	.	.	.
Madras	.	.	.	.	25,340
Bombay	.	.	.	.	135,658
Pargana Manpur	.	.	.	.	47

Corresponding data for the American linseed crops in 1907 and 1911 are given in the following tables :—

American Linseed Crop in 1907

State.	Acres.	Average Yield per Acre	Total Yield.
		Bushels	Bushels
North Dakota	1,700,000	8·0	13,602,000
South Dakota	480,000	10·0	4,800,000
Minnesota . . .	474,000	10·5	4,978,000
Total for three N.W. States	2,654,000	9 5	23,380,000
Wisconsin	36,000	14·2	515,000
Iowa	20,000	11·5	235,000
Missouri . . .	30,000	10 0	305,000
Nebraska . .	16,000	11·0	174,000
Kansas	54,000	10·0	539,000
Oklahoma	6,000	15·0	90,060
Montana	34,000	13 0	436,000
Idaho . . .	14,000	13·0	177,000
Total for United States .	2,864,000	9·0	25,851,000

American Crop of Linseed in 1911

State.	Acres	Average Yield per acre	Total Yield.
		Bushels.	Bushels.
Colorado	3,000	7·0	21,000
Iowa	16,000	8·0	128,000
Kansas	75,000	3·0	225,000
Minnesota	400,000	8·0	3,200,000
Missouri	18,000	3·0	54,000
Montana	425,000	7·7	3,272,000
Nebraska	2,000	5·0	10,000
North Dakota	1,200,000	7·6	9,120,000
Oklahoma	1,000	3·0	3,000
South Dakota	607,000	5·3	3,217,000
Wisconsin	10,000	12·0	120,000
	2,757,000	7·0	19,370,000

Physical and Chemical Characteristics of Linseed Oil

Specific Gravity		Solidifying Point.		Melting Point		Saponification Value		Iodine Value [4]		Reichert-Meissl Value.	
At °C.	Observer	°C.	Observer.	°C	Observer	Mgrms KOH	Observer	Per cent	Observer.	c c ½ Norm. KOH	Observer.
12	0 939	Saussure	at −25 "stearine" deposits	Lewkowitsch	−16 to −20	Glaessner	190 2–192 7	De Negri and Fabris	170–204 See Table p 63	Lewkowitsch p 63	0 00	Crossley and Le Sueur[2]
15	0·932- 0·937	Allen					192 2–195 2	Lewkowitsch	194 0	Thomson and Dunlop[3] Wijs[4]		
"	0·9342	De Negri and Fabris					194 5	Crossley and Le Sueur[2]	176 3–201 8			
15·5 (water at 15·5=1)	0·9316- 0·9410	Lewkowitsch[1]							205 4	Thomson and Dunlop[5] Grimme		
"	0·931-	Gill and Lamb							194 25			
"	0 938	Crossley and Le Sueur[2]							194 67			
"	0·9337	Allen										
99 (water at 15·5=1)	0·8809											

1 Cp. table, p. 63
4 Cp. table, p. 64.

2 East Indian oil from the Central Provinces.
5 From packed Baltic (Riga) seed (*Analyst* 1906, 252)

3 North American Oil (*Analyst* 1906, 252)
6 China linseed, brown.
7 China linseed, yellow.

Physical and Chemical Characteristics of Linseed Oil—continued

Thermal Tests.

Maumené Test.		Heat of Bromination.	
°C.	Observer.	°C.	Observer.
103	Maumené	30.4-31.8	Hehner and Mitchell
104-111	Allen	31.4-32.51 2	Archbutt
122-126	De Negri and Fabris	29.8-30.51, 3	,,
90-106.5	Gill and Lamb	30-33	Bromwell and Meyer6
128-145	Archbutt		
Specific Temperature Reaction.			
320 to 349 313	Thomson and Ballantyne Jenkins		

Refractive Index.

At °C.		Observer.
15	1.4835	Strohmer
20	1.4800-1.4812	Harvey
60	1.4600	Thoerner

Oleo-refractometer.

At °C.	"Degrees."	Observer.
	+48 to +53	Jean
	+48 to +52	Bruyn and van Leent
22	+50 to +54	Permain

Butyro-refractometer.

At °C.	"Degrees."	Observer.
20	84-90	Lewkowitsch7
25	81-87	White4
40	74.5	Crossley and
,,	72.5	Le Sueur4

Viscosity.

Seconds at 70° F.	Observer.
211.7	Crossley and Le Sueur4

1 The ... of temperature observed multiplied by two, as 0.5 gm of oil only was used
3 East India oil. 4 East India oil from the Central Provinces. 2 Baltic oil.
5 North American oils, *Journ. Soc. Chem. Ind.*, 1899, 282. The corresponding oils had the iodine values 166-180   160 is decidedly too low
for a genuine American oil 6 *Amer. Journ. Pharm.* 1897, 145
7 Six oils described, *Chem. Revue*, 1898, 211 (cp. table, p. 63). 8 *Journ. Soc. Chem. Ind.*, 1900, 1089.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Fatty Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.		Ether-insoluble Bromides.[5]	
Per cent.	Observer.	At °C.	Observer.	°C	Observer.	°C	Observer.	Mgrms KOH	Observer.		Observer.	Per cent	Observer.	At 40° C.	Observer.	Per cent	Observer.
94·81	Crossley Le Sueur[1]	15·5	Allen	13·3	Hubl	17	Hubl	198·8	Dieterich	283	Williams	179· 200·8	Lewkowitsch (Cp p 53)	1·4546	Thoerner	29 1- 31·3	Walker and Warburton
95·5 (mean value)	Lewkowitsch	99 (water at 15·5=1)	,,	16-17	De Negri and Fabris	20- 21	De Negri and Fabris	196	Thoerner							30- 41·9	Lewkowitsch[6]
		0·9233									Cp Fahrion, Chem Zeit 1907. 484						
		0·8612										Liquid Fatty Acids.				Liquid Fatty Acids
		0·8925	Archbutt		Titer Test											34·9	Walker and Warburton
		100 (water at 100=1)		19·0- 19·4 20·2- 20·6	Lewkowitsch ,,							204·4 Tortelli and Rüggeri[2] 189·1- 193 199·8 Lewkowitsch[4]					

[1] East India oil from the Central Provinces.   [2] Cold-pressed oil, of iodine value 179·4.

[3] Italian oils, 1898 and 1899 crop, of iodine values 173·4-176·8.   [4] East Indian oil, iodine value 184

[5] Erdmann and Bedford, *Zeitsch. f. physiol. Chem.*, 1910(69), 77, give 43·4 per cent for petroleum-ether washed hexabromides. The washing with petroleum ether is decidedly wrong, as tetrabromides may have remained on the filter. Eibner and Muggenthaler found by their method (see Vol. I Chap. VIII) much higher numbers.   [6] Unpublished results.

Two qualities of **Russian** seed are recognised in the trade, they are known, according to their source, as Baltic and Black Sea seed ; hence the terms " Baltic linseed oil " and " Black Sea linseed oil." The oil expressed from Indian seed is known as " East India oil." Baltic linseed yields the best drying oil ; this is to some extent explained by the fact that the Baltic seed is the purest, whereas in Black Sea seed 5 per cent (and more) of hemp seed or ravison seed are usually present, and Indian seed is always mixed with mustard, rape, and cameline seed, owing to the plants yielding the latter being grown along with the flax plant. It has been proved that when the Indian linseed is carefully separated from the foreign seeds and then expressed, the oil possesses as good drying properties as best Russian oil. During latter years, more attention having been paid in India to this important industry, the quality of seed has improved. Argentine seed, yielding the River Plate oil (La Plata oil), used to contain much chaff and admixed fibres, owing to careless treatment in harvesting. Since farmers have begun to apply greater care, the Argentine linseed comes now into the market in a much improved condition, so that not infrequently seed is returned as " 98-99 per cent clean " linseed. Nevertheless, possibly in consequence of the climatic conditions or the " race " of the seed, the Argentine oil does not approach in quality (" richness ") either Baltic or Indian oil. North American oil ranks almost on a par with Argentine oil (cp. also below, iodine values) ; in this case also the quality of the oil depends to a considerable extent on the purity of the seed. Canadian linseed having been reared from Baltic seed (imported for this purpose) yields an oil equalling in quality Baltic linseed oil. Hence Canadian linseed oil is much superior to North American linseed oil.

An indication as to impurities occurring in commercial seeds is furnished by the following table due to *E. J. Sheppard.*[1]

	Original Seed			Picked Seed		
Kind of Seed.	Oleaginous Impurities, per cent.	Non-Oleaginous Impurities, per cent	Oil in Total Impurities, per cent.	Oils per cent	Sp. Gr. at 15.5/15.5° C	Weight of one Seed, in mgrms.[2]
1. American	1.50	1.69	10.0	39.67	1.1388	4.61
2. American	1.01	1.05		39.40		4.53
3 La Plata	0.58	5.64	14.1	36.98	1.1415	5.58
4. Calcutta	4.85	5.03	14.9	40.82	1.1326	5.41
5. Bombay	0.81	2.80		41.23	1.1182	7.88
6. S. Russia (Kertch)	5.05	1.71		39.11	1.1375	5.74
7. N. Russia (Riga)	3.31	1.97		36.95	1.1458	4.19

Linseed arriving in this country is sampled and tested by the *Incorporated Linseed Association,*[3] who ascertain the proportions of linseed and foreign seeds ; oil-yielding seeds other than linseed are reported as having half the value of the latter, whereas non-oleaginous seeds are considered as valueless.

[1] *Journ. Ind. Eng. Chem.,* 1912 (4), 14.
[2] Average of 4000 full-sized seeds.
[3] This Association has recently joined an International Committee of European oil millers.

Recently Chinese linseed has been placed on the market under the commercial name of Chinese linseed, yellow, and Chinese linseed, brown. The quality of the oils obtained therefrom characterises the seed as a good linseed. The iodine values of the oils have been given in the table of characteristics.[1]

The proportion of linseed oil in the seed varies with the origin of the seed,[2] and also with the seasons. The figures given below should therefore only be considered as average numbers. It should also be remembered that on extracting seeds with ether larger quantities of crude oil are obtained than on extracting with petroleum ether.

Proportion of Oil in Seeds

		Per cent.
Russian linseed	. . . . .	32-38
Indian ,,	. . . . .	37-43
River Plate ,,	. . .	35-36
N American ,,	. .	36-38
Levant ,,	. . .	37-42
Hungarian ,,	. . . .	36-38
Morocco ,,	.	36-40
Sicilian ,,	. . . .	41-42
Chinese ,, (yellow-brown)	. . .	31-38

Some details regarding the yield of linseed oil from seeds derived from different districts of East Indies are supplied in the following table :—

District	No. of Samples.	Oil per cent	Weight of 100 Seeds.
			Grms.
Punjab	10	35·60-41 91	0·286-0·630
Central Provinces . .	21	36·47-43·93	0·520-1·029
Bombay Presidency	7	41·23-44·45	0·669-0·888
Madras Presidency .	5	40·46-41 71	0·660-0·703
United Provinces .	9	41·44-44·55	0·537-0·923
Bengal . .	1	41·40	0·516
Assam . . .	1	42·06	0·521

[1] C. Grimme, *Chem. Revue*, 1912, 280.

[2] Experiments made in India with linseed rich in oil and taken to farms where usually seed yielding a smaller proportion of oil was grown, showed that there was a decline in the percentage of oil. The following table shows some results of those experiments :—

	Original Seed.	Produce of 1905.	Produce of 1906.
Linseed White from Cawnpore . .	44·62	41·28	39·90
,, ,, ,, Khandwa .	44·96	44·18	42·93
,, ,, ,, Damoh .	45·34	43·07	43·57
,, . Brown from Partabgarh	43·17	40·98	38·31
,, ,, ,, Cawnpore . .	42·05	40·97	39·48
,, ,, ,, Sholapur . .	41·13	40·42	38·82

(*Memoirs of the Department of Agriculture in India,* by J. Walter Leather, vol. i. No. 2, p. 38.)

The quantity of linseed oil produced per annum may be taken as being about 35 per cent of the seed; hence the total world production of linseed oil can be gathered from the above given tables. The production of linseed oil in this country is detailed in the following table. The considerable falling off in the production during 1910 and 1911 was caused by the abnormally high prices of linseed.

Production of Linseed Oil in the United Kingdom

Year	Barrels of 40 gallons
1902	102,817
1903	128,651
1904	168,506
1905	115,137
1906	95,380
1907	124,179
1908	127,390
1909	101,079
1910	78,688
1911	81,113

The German imports and exports of linseed oil are detailed as follows :—

German Imports and Exports of Linseed Oil

(In metric tons)

Imports		1911.	1912.	Exports.	1911.	1912.
From Belgium	. .	81	233	To United Kingdom .	2041	271
,, Holland	. .	2420	2554	,, Austria-Hungary .	297	196
,, Russia .	. .	140	199	,, Brazil . . .	206	199

On pressing linseed in the cold, a golden-yellow coloured oil is obtained, which has a pleasant taste, so that it can be used as an **edible oil**. Considerable quantities are being expressed for this purpose in Russia, Hungary, Germany, and India. In some parts of Germany, the oil is used either as such (as " Leinölschmalz ") or in admixture with tallow or (and) lard for edible purposes. Such linseed oil is refined by filtering over fuller's earth.

By far the largest quantities of oil are, however, employed in the arts. In that case the seed is crushed between rollers and heated up to about 160° F. in the mixing kettle; subsequently the seed is expressed whilst still warm. The oil so obtained has a yellowish-brown hue and is somewhat turbid, due to traces of moisture and mucilaginous matter. The press cakes retain about 10 per cent of oil.

The press cakes are used as one of the most valuable and wholesome

cattle foods.[1] It should, however, be noted that they contain a small quantity of a cyanogenetic glucoside, linamarin,[2] which has been shown to be identical with phaseolunatin [3] (a dextrose ester of acetone cyanohydrin), and an enzyme occurring naturally in linseed and in the flax plant. In the presence of water this enzyme acts on the glucoside with production of prussic acid.[4] The temperature to which the linseed meal is heated, preparatory to pressing, suffices to destroy the enzyme. Hence linseed cake as found in commerce is innocuous to the cattle. Cases of cattle poisoning after feeding with linseed cake were, as a rule, hitherto ascribed to an admixture with poisonous seeds, such as castor seed. In the light of the foregoing facts the poisoning may, however, have been due to prussic acid, generated from the cyanogenetic glucoside in consequence of too low a temperature having been employed accidentally in the process of expressing the oil. For this reason the meal obtained in *Anderson's* press (see p. 15) should not be fed to the cattle.

Under the name " Calcutta linseed cake," *native-made cakes* are imported into Europe which by no means represent what the name suggests. A number of such cakes which the author had occasion to examine consisted to the extent of about one quarter only of genuine linseed cake, whereas the remainder was formed by mowrah cake.[5] An analysis of a cake of this kind by the author gave the following results :—

	Per cent.
Oil	9·45
Nitrogen	4·740
Albuminoids	29·68
Ash	8 97
Moisture	8·69
Wood fibre	14·09
Common salt	0·279
Carbohydrates by difference	29·12

The oil extracted from the cake gave the following numbers :—

	Per cent.
Iodine value	88·10
Free fatty acids	75·00
Neutral fat	25·00
Melting point of fat	30·0 to 32·2° C.
Melting point of total fatty acids	40·6 to 47·2° C.

In consequence of the greatly extended production of sesamé cake (owing to the great demand for sesamé oil in the margarine industry), sesamé cake is fraudulently admixed to linseed cake. The microscopical examination reveals the admixture.

[1] For the examination of linseed cakes cp. E. Collin, *Journ. Pharm. Chim.*, 1909 (vi.), 256 ; also L. Vuaflart, *Ann. des falsif.*, 1911, 381.

[2] Dunstan, Henry, and Auld, *Proc. Royal Soc.*, 1906, 78, 145. Cp. also C. Ravenna and M. Zamorani, *Atti dell' Accad. dei Lincei*, 1911 (5), ii. 356 ; S. H. Collins, *Journ. Soc. Chem. Ind.*, 1912, 507.

[3] During germination of *phaseolus lunatus* no hydrocyanic acid is liberated by the action of the enzyme. Guignard, *Compt. rend.*, 1908, 1023.

[4] Henry and Auld, *Journ. Soc. Chem. Ind.*, 1908, 428.

[5] Cp. also Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1910, 1432.

A. Gregroire and E. Carpiaux [1] base a method of detecting sesamé cake on the fact that pure sesamé cake contains about 2½ per cent of calcium oxide as against about 0·43 per cent in linseed cake.

On storing the oil, the moisture and the mucilaginous matter gradually settle out, and the oil thereby acquires a higher value, especially for some technical uses, as in the making of varnish. Such oil, sometimes kept for years, is known as " tanked oil." The suitability for varnish-making purposes is ascertained rapidly by heating the linseed oil in a test-tube. Oil from which gelatinous matter separates is considered unsuitable. Seed expressed in a comparatively fresh (" green ") state yields oil containing larger quantities of " mucilage " than seed three to six months old. The gelatinous matter, " mucilage " or " spawn " or " break," contains phosphates and traces of sulphates. *G. W. Thompson* [2] found that a sample of freshly expressed linseed oil heated to 400° F. yielded 0·277 per cent of a precipitate. On washing it with petroleum ether to remove the oil completely, this foreign substance gave 47·79 per cent of ash (0·1177 per cent of the original oil), consisting of 20·96 per cent calcium oxide, 18·54 per cent magnesium oxide, 59·85 per cent phosphorus pentoxide, and traces of sulphate. Other specimens of linseed oil gave the following results :—

Description.	Ash. Per cent
1. Fresh double-filtered raw American linseed oil	0·1429
2. ,, ,, ,,	0·1967
3. Good well-settled ,, ,,	0·0609
4. Best American linseed varnish oil ,,	Traces

In my own practice I have met with linseed oils containing as much as 0·2 per cent of ash. Such oils give a notable amount of mucilage.

The following analyses of " Ether-Insoluble Mass," obtained from " foots," [3] may prove of interest :—

	Linseed Oil "Foots," from Oil prepared by Hydraulic Pressure	Linseed Oil "Foots," from Oil prepared by Extraction with Naphtha.		Linseed Oil "Break," obtained from Naphtha-extracted Oil, by heating to 500° F. with Superheated Steam.
	Per cent.	Per cent.		Per cent.
		I.	II.	
Silica	nil	12·53	34·38	0·25
Manganese oxide		0·51	7·98	1·00
Lime	3·26	3·17	8·39	23·53
Magnesia	4·99	6·25	46·50	14·51
Phosphorus pentoxide	81·08	72·75	.	60·30
Sulphuric acid				none
Potash	10·27	present		..

[1] *Bull. Soc. chim. de Belgique*, 1912 (26), 479.

[2] *Journ. Soc. Chem. Ind.*, 1903, 1005.

[3] Collated from notes by O. Eisenschimë and H. N. Copthorne, *Journ. Ind. and Eng. Chem.*, 1910, 29.

E. W. Boughton [1] found in sixteen specimens of raw linseed oil traces of manganese (up to 0·0008 per cent).

The bulk of linseed oil is at present produced by expression. The main reason for this is that the hot-pressed cake is valuable as cattle food, whilst linseed meal obtained by extraction with solvents could only be used as manure, at any rate in this country.[2] In the United States of America some linseed is extracted with solvents (naphtha), as it is thought that the oil so obtained, being richer in unsaturated acids, and containing less mucilaginous matter, would be more suitable for the oil and paint trade. This has, however, not been borne out by practice, extracted oil having been found unsuitable as a paint oil (cp. Vol. III. " Paint Oils "). Moreover, the oil obtained by extracting with carbon bisulphide, petroleum ether, etc., possesses inferior colour and a more unpleasant smell than expressed oil.[3] Therefore it would only be profitable to extract damaged seed, which does not yield proper cattle food.

As mentioned already, the impurities settle out on long standing, especially in the cold,[4] and the enhanced value of " tanked oil " consists in the comparative freedom of such oil from foreign substances. A more rapid method of removing these impurities is to refine the oil, as in the manufacture of " paint oils." The process consists in treating linseed oil with 1 to 2 per cent of somewhat concentrated sulphuric acid. The charred mass carries down with it the bulk of impurities contained in the crude oil. For the manufacture of the best and finest kinds of linseed oil —"artists' oil"—the seed is pressed in the cold, and the refined oil is subjected to " sun-bleaching," by exposure in shallow zinc trays under glass to the action of sunlight. Powdered lead placed in the trays accelerates the bleaching process. *Genthe* [5] proposes to bleach linseed oil by exposure to the *Cooper Hewitt* mercury lamp, whilst a current of air is pressed through the well-agitated oil.[6] (Cp. Vol. III. " Boiled Oils.") Dark linseed oils intended for soft soap are usually bleached in the soap works themselves by treatment with a small amount of caustic potash. The soap which is formed carries down with it colouring matters.

A number of patents have been taken out for the refining of linseed oil by means of ozone ; the writer examined several processes worked on a semi-large scale, but none of them can be said to have superseded the usual methods.—Attempts made by the author to remove the solid glycerides from linseed oil on a commercial scale, with a view to obtaining an oil of still higher drying power than is possessed by refined oils,

[1] *Journ. Ind. and Eng. Chem.*, 1913 (5), 282.

[2] The German Agricultural Associations distinctly exclude by their specifications cakes containing extracted meal. Such meal is exported to Europe under the name of "Cleveland meal" (see p. 28).

[3] Cp. Mitarewski, *Chem. Zeit. Rep.*, 1906, 241.

[4] Cp. Niegemann's German patent 163,056, p. 31.

[5] German patent 223,419. Cp. Flatt, *Farben-Zeitung*, 1907, 108.

[6] Cp. also German patent 11,213, 1880, Cattanach. Linseed oil is also bleached with potassium bichromate in hydrochloric acid, bleaching powder, etc., but as it is difficult to remove the last traces of chemicals these processes are not practised frequently.

have not proved successful. The value of the method patented by *Hertkorn*[1] for achieving the same object appears therefore rather doubtful.

The chemical composition of linseed oil is but imperfectly known. *Mulder* was the first to state that the oil contains about 10 per cent of glycerides of solid fatty acids, consisting of palmitic and myristic acids in about equal proportions. The solid acids separated from the liquid acids by means of the lead-salt-ether method contained, however, notable quantities of liquid acids. *Tolman and Munson*[2] found by the same method only 3·88 per cent of solid acids. The total fatty acids can be distilled *in vacuo* without undergoing decomposition, but they cannot be thus separated from each other. *Haller*[3] showed (by fractional distillation of the ethyl esters of linseed oil, see Vol. I. Chap. XII.), that amongst the solid acids of linseed oil also stearic acid occurs in appreciable proportions, and arachidic acid in very small quantities. It may be pointed out that the iodine values of the linseed oils examined by *Haller* varied from 168 to 175. These numbers are somewhat low, and it would therefore appear that linseed oils of higher iodine values must be poorer in solid acids.

The earliest statement by *Hazura and Grüssner*, that the fatty acids of linseed oil consist of 5 per cent of oleic acid, 15 per cent of linolic acid, 15 per cent of linolenic acid, and 65 per cent of " isolinolenic " acid, allowing as a *maximum* 10 per cent of solid acids, would lead to a much higher iodine value than actual experiments warrant. This is shown by the following calculation. A mixture of fatty acids having the following composition :—

					Per cent
Solid acids	.	.	.	.	10
Oleic acid	.	.	.	.	4·5
Linolic acid	.			.	13·5
Linolenic acid	.			.	13·5
" Isolinolenic " acid[4]	.	.	.	.	58·5
					100·0

should absorb, theoretically, 225·89 per cent of iodine. The liquid fatty acids, freed from solid acids, should therefore have the calculated iodine value of 250·9, whereas the highest number found in my laboratory for the liquid fatty acids (prepared by *Tortelli and Ruggeri's* method) was only 210. To explain the discrepancy *Fahrion* assumed that raw linseed oil is polymerised during the process of manufacture. This assumption, however, cannot be substantiated.

From the percentage of ether-insoluble bromides, 41·9 per cent, I found (see table, p. 53) the calculated proportion of linolenic acid is 15·4 per cent only, since 100 parts of hexabromide correspond to 36·68

[1] German patents 129,809 and 137,306 ; cp. *Jahrbuch der Chemie*, xii. 370.
[2] *Journ. Amer. Chem. Soc.*, 1903, 960.
[3] *Compt. rend.*, 1906 (146), 259.
[4] The existence of isolinolenic acid must also be doubted, see Vol. I. Chap. III.

parts of linolenic acid. This amount may be below the true one, but
the deficiency is not sufficiently explained by assuming that some
ether-insoluble bromide was dissolved together with linolé tetrabromide;
for experiments which I made with varying amounts of bromine and
ether did not lead to results differing materially from the above-named
percentage of ether-insoluble bromide, viz. 41·9 per cent under the
experimental conditions described in Vol. I. Chap. VIII. p. 570. The
following is an account of an examination of a specimen of linseed oil
carried out in my laboratory :—The sample had the iodine value
190·4, it yielded 37·72 per cent of ether-insoluble brominated glycerides,
and 8·9 per cent of solid acids of the iodine value 22·3 (by the lead-
salt-ether method[1]). After passing the solid acids once more through
the same process, 7·5 per cent of solid fatty acids of the iodine value
19·2 were obtained. The mixed fatty acids had the iodine value 194·4,
and yielded 38·1 per cent of ether-insoluble bromide of the melting
point 176·4° C. Attempts to obtain further quantities of insoluble
bromides from the ethereal filtrate failed (cp. Vol. I. Chap. VIII. p. 571).
The amount found, calculated to hexabromide, leads to 14 per cent
of linolenic acid. But even on the assumption that linseed oil contains
no oleic acid –the dihydroxystearic acid obtained by *Hazura* being
regarded as a product of secondary reaction –the iodine value of the
mixed fatty acids would only come to 182·2, as shown by the following
calculation :—

	Per cent.	Iodine Value.
Solid fatty acids of the iodine value 19·2	7·5	1·4
Linolenic acid . . .	14·0	38·4
Linolic acid, by difference . .	78·5	142·4
		182 2

whereas experiment led to 194·4.

This would show that the percentage of linolenic acid is taken too
low. Whether this be due to part of the hexabromide having remained
in the filtrate or whether, according to *Rollet's* theory, only one-fourth
of the hexabromides has crystallised out, must be left open to doubt.
Tested by *Rollet's* theory, the last table would work out as follows :—

	Per cent.	Iodine Value.
Solid fatty acids of the iodine value 19·2 .	7·5	1·4
Linolenic acid	56·0	153·0
Linolic acid, by difference . . .	36·5	66·06
	100·0	220·46

[1] By precipitation with lithium acetate Fahrion obtained an acid of iodine value
22·5 ; yield 7 per cent (*Zeitschr. f. angew. Chem.*, 1904, 1484).

The last figure would be too high ; it might be reduced by assuming that there is some oleic acid present which would reduce the percentage of the linolic acid and thus bring down the iodine value. If, on the other hand, *Rollet's* theory be rejected, and *Erdmann and Bedford's* figures be accepted, viz. that the most unsaturated acids consist of 78 per cent of linolic acid and 22 per cent linolenic acid as derived from the hydrogen value of the mixed liquid fatty acid, and allowing no oleic acid, we should have the following calculation :—

	Per cent	Iodine Value.
Solid fatty acids of the iodine value 19·2 .	7·5	1·4
Linolenic acid	20·35	55·76
Linolic acid	72·15	130·59
	100·0	187·75

which is again too low.

Accepting the result found by *Eibner and Muggenthaler* (Vol. I. Chap. VIII. p. 573), viz. that linseed oil yields about 50 per cent of hexabromide, this would lead to a calculated figure of 21 per cent of linolic acid, and thus bring back the calculation approximately to the last one embodying *Erdmann's and Bedford's* results.

Fahrion gave the composition of a linseed oil, of the iodine value 173·2, in the following round numbers, to which the author has added the corresponding iodine values.

	Per cent.	Iodine Value	Calculated Iodine Absorption.
Solid acids . . .	8·5	6·8	0·58
	0·8	11·5	0·09
Oleic acid . . .	17·5 (approx.)	90	15·75
Linolic acid . .	30·0 (approx.)	181	54·42
Linolenic acid . .	38·0 (approx.)	274·1	104·16
	94·8		175·04

The proportion of oleic acid was based by *Fahrion* on the fact that a certain percentage of dihydroxystearic acid was obtained which was again calculated—on the basis of an assumed yield of 60 per cent—to oleic acid.   There is, however, proof wanting that the dihydroxystearic acid found owes its origin entirely to oleic acid.   The proportions of linolic and linolenic acids were derived from a method of oxidising the fatty acids on cotton wool.   As this method must be considered a very hazardous one, the agreement of the calculated iodine value with the iodine value of the linseed oil cannot be considered as supporting the calculation, and no definite conclusions can be derived, in the author's opinion, from this analysis as to the actual occurrence of linolic acid in linseed oil.

It is evident that further researches are required satisfactorily to establish the composition of the linseed oil fatty acids.[1]

By catalytic reduction with hydrogen, linseed oil can be converted into completely saturated glycerides. *Paal and Roth* [2] obtained by using palladium as a catalyst a brittle mass, melting at 61-65° C.

On exposure to air in a thin film on a large surface linseed oil readily absorbs **oxygen**, and dries to a neutral substance, insoluble in ether (or practically insoluble in ether, for according to *Fahrion*, it passes almost completely into solution when treated with a large quantity of ether during one year, with frequent shaking). This substance, the nature of which has not been ascertained hitherto, is termed "linoxyn," and is stated in its turn to be further oxidised to a liquid substance —superoxidised oil (cp. Vol. III. Chap. XV. "Oxidised Oils").

The ready absorption of oxygen explains the occurrence of small amounts of "oxidised" acids in even comparatively fresh linseed oils. When kept protected from moisture, air, and light, linseed oil keeps indefinitely, as shown by the following table, which contains the proportions of "oxidised" acids in some (comparatively) fresh and old linseed oils examined by *Lewkowitsch* [3] (together with a few other "characteristics" and "variables") :—

	"Oxi-dised" Acids.	Specific Gravity At 15·5 C (water 15·5=1)	Butyro-re-fractometer "Degrees" At 20° C.	At 25°C	Saponific Value.	Iodine Value.	Acid Value.	Unsapour-fiable.
	Per cent							Per cent.
Oil from finest Calcutta seed, 2 months old . . .	0·65	0·9316	84	82	193·2	170·46	1·3	0·65
Oil from finest Calcutta seed, 3 years old, kept the whole time protected from air and light .	0·7	0·9324	84	81	192·5	174·0	1·3	0·7
Finest St. Petersburg seed, 3 months old	0·88	0·9334	86·5	84	192·2	177·3	1·3	1·1
Finest St. Petersburg seed, 7 months old	0·56	0·9345	87	84	193·1	176·2	1·3	0·98
Baltic (commercial) seed, containing ravison and cameline seed	0·73	0·9343	86·5	84	194·3	170·1	1·3	1·1
Finest and purest Baltic seed, kept 13 years protected from air and light . . .	1·95	0·9410	90	87	195·2	175·8	7·2	1·1

As will be gathered from the preceding table, the proportion of free fatty acids in linseed oil is as a rule small; it rarely exceeds in good commercial samples 1-1·5 per cent. The acetyl value of linseed oil was found by *Lewkowitsch* 3·9. The proportion of unsaponifiable matter varies in commercial samples from 0·3 to 1·2 and even 2 per

[1] Cp. also Vol. I. Chap. VIII.
[2] *Berichte*, 1909, 1550.
[3] *Journ. Soc. Chem. Ind.*, 1899, 51 ; *Chem. Revue*, 1898, 211.

cent (in River Plate oil), the amount depending on the care with which the manufacture has been carried out [1] in the press-room. If the piston of the hydraulic press works in mineral oil, contamination with the latter may easily take place. The unsaponifiable matter contains phytosterol, but no stigmasterol [2] (difference from rape oil).

On heating linseed oil to 250°-300° C. the specific gravity increases considerably owing to the formation of polymerisation products (see Vol. III. Chap. XV. " Polymerised Oils ").

The United States Government specifications for linseed oil (August 15, 1912) are as follows :—

The oil must be strictly pure, well-settled linseed oil, perfectly clear, and not show any deposits of " foots " or a loss of more than 0·2 per cent, when heated for one half-hour to a temperature of from 103° C. to 105° C. ; it must show on examination the following characters :—

	Maximum.	Minimum.
Specific gravity at 15° C.	0·936	0·932
Specific gravity at 25° C.	0·931	0·927
Iodine value (Hanus)	190	178
Saponification value	192	189
Acid value	3	
Refractive index at 25° C.	1·4805	1·479
Unsaponifiable matter . . . per cent	1·5	

The oil, when poured on a glass plate and allowed to drain and dry in a vertical position, guarded from dust and exposure to weather, must dry free from tackiness in less than 75 hours at a temperature of from 15·5° C. to 26·5° C.

The following tests will be found sufficient for the examination of a sample :—

Specific Gravity.—Linseed oil has a higher specific gravity than any fatty oil that would be used to adulterate it, with the exception of tung oil. Hence a lower specific gravity than 0·93 in a given sample would direct attention to the presence of other fatty oils or mineral oils. A higher gravity would indicate probable adulteration with rosin oils. The presence of " boiled linseed oil," which has a higher specific gravity than linseed oil, would in the first instance be detected by the specific gravity test.

The higher the specific gravity of a linseed oil, the more suitable it is for the purposes of the paint and varnish manufacturer. This is also expressed in a general way by the magnitude of the iodine values. Thus *Wijs* [3] has shown that the specific gravities of a number of linseed

[1] In a number of determinations of the unsaponifiable matter in linseed oils of different origin carried out by Niegemann (*Chem. Zeit.*, 1904, 97), the percentages varied from 0·83 to 2·1 per cent. Cp. Fendler, *Deut. Pharm. Ges.*, 1904, 149 ; Niegemann, *Chem. Zeit.*, 1904, 830 ; Thoms and Fendler, *ibid.*, 1904, 841 ; Niegemann, *ibid.*, 1904, 885 ; F. Lorentz, *ibid.*, 1904, 819.

[2] *Berichte*, 1907, 3682.

[3] *Chem. Revue*, 1899, 29 ; *Journ. Soc. Chem. Ind.*, 1899, 591.

oils varied from 0·9310 to 0·9352 as their iodine values varied from 180·1 to 200. On storing (" tanking "), the specific gravity increases, as shown by the numbers recorded in the last given table.

The increase must be ascribed to a slight oxidation of the oil, due to the absorption of oxygen, and not to polymerisation.

Iodine Value.—Linseed oil has, with the exception of perilla oil, the highest iodine value of all known fatty oils. Hence the iodine test is the most characteristic one for identifying a sample. The iodine numbers given by earlier observers are much too low, owing to too small an excess of iodine solution having been used ; those values have therefore not been recorded in the above given tables. Correct iodine values are obtained by allowing the *Hübl* iodine solution to act eighteen hours ; on using the *Wijs* iodine solution six hours suffice. In either case an excess of iodine must be present, about equal to the quantity of iodine absorbed.

If the iodine value of a sample falls below 170, the presumption that the sample has been adulterated is justified. Lower iodine values have been found occasionally in " genuine " linseed oils, but the adulteration may have taken place in the seed itself, as it were, the oil having been produced from impure or adulterated linseed (see below). Oils bleached with bichromate and hydrochloric acid absorb less than 150 per cent of iodine.

Somewhat lower values than those given in the table may also be due to an oil having been exposed to the atmosphere, and thereby having absorbed oxygen. This point must be borne in mind before a sample can be pronounced adulterated, as purity of an exposed oil is quite consistent with a somewhat low iodine value.

A high iodine value of itself is, however, not proof of purity, since other drying oils, fish oils, and rosin oils may be admixed with linseed oil in considerable quantities, and yet furnish numbers lying in the neighbourhood of those given in the table of characteristics.

The following table, containing the iodine values of linseed oils from specified sources, will be found useful :—

[TABLE

Kind of Linseed.	Iodine Value of Oil.[1]	Observer.
Baltic . .	190-201	Lewkowitsch [2]
. . . . . .	190-204	Ingle
Archangel, Wiatka, Petersburg, Reval,		
Pernau, Riga, Libau . . .	188·5-200	Wijs
Central Russia (Samara, Steppes) .	188·9-189·1	,,
Black Sea, Asoff; Taganrog . .	176·3-182·5	,,
Black Sea	176-182	Ingle
East India	170-190	Lewkowitsch
,, ...	182·2-187·5	Wijs
River Plate . . .	180-189	Ingle
,, . . .	174·7-182·7	Wijs
,, . . .	179-191	Lewkowitsch
,, . . .	175-186	Ingle
Dutch . . .	191·5-201·8	Wijs
Commercial . . .	181·5	Ingle
North America . . .	178·1-188·5	Wijs
,, ,, . . .	194-194·6	Thomson and Dunlop
,, ,, . . .	177-188	Ingle
Danube countries . .	182·1	Wijs
Chinese	191	Grimme
Mixed Linseed : from—		
Dutch and Baltic	199·1	Wijs
Various Baltic seeds . . .	198·1	,,
⅔ Baltic and ⅓ Dutch . . .	195·7-197·5	,,
½ ,, and ½ ,, . . .	195·1-195·4	,,
⅔ Black Sea and ⅓ Baltic . .	185·5	,,
¹⁄₅ ,, and ⁴⁄₅ River Plate .	183·7	,,
½ Black Sea, ¼ River Plate, ¼ East		
India, ⅓ North America . .	183·3	,,
½ La Plata, ¼ East India, ⅓ Black Sea	183·2	,,
½ ,, ¼ ,, ¼ ,,	182·9	,,
⅔ East India, ⅓ Black Sea .	182·7	,,
Black Sea and East India . .	181·5	,,
Black Sea, and East India, and North		
America	181·1	,,
½ Black Sea and ½ East India .	180·9	,,
⅔ River Plate and ⅓ East India .	180·1	,,
River Plate, Black Sea, East India .	178·7	,,

Bromide Test.—This is an important test for purity. Pure linseed *oils* yield up to 38 per cent of crude ether-insoluble brominated glycerides. From the table given in Vol. I. Chap. VII. it will be gathered that all other drying oils such as tung oil, poppy seed oil, safflower seed oil, candle nut oil, soya bean oil, either yield much smaller quantities or no ether-insoluble brominated glycerides. If a sample yield less than 20 per cent brominated glycerides, the presence of other oils may be inferred with certainty. It is much preferable, however, to brominate the mixed fatty acids (prepared with due precaution against oxidation),

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[1] During recent years greater care is taken in all linseed-producing countries to market purer seed than was obtained previously (see above, p. 54).

[2] Cp. also table, p. 63.

and to isolate the linolenic hexabromide. Linseed oil mixed fatty acids yield (by the method described Vol. 1. Chap. VIII. p. 570) up to 42 per cent of bromide, melting from 175° to 180° C., whereas all other drying (vegetable) oils give much smaller quantities (cp. Vol. 1. Chap. VIII. p. 571).

Since fish, liver, and blubber oils also yield high percentages of insoluble bromo-products in the bromide test—*octo-bromide*—the determination of the melting point of the bromides must not be omitted. Linolenic hexabromide from drying oils melts at 175°-180° C. to a *clear liquid*, whereas the octobromides from fish, liver, and blubber oils do not melt at these temperatures, being converted at about 200° C. into a black mass. Experiments carried out in my laboratory proved that it is thus possible to detect admixtures of 10 per cent of fish oil with linseed oil. (Vol. 1. Chap. VIII. p. 571.)

Eibner and Muggenthaler's method yields much higher proportions of hexabromide than given above ; these authors find in a number of linseed oils the following proportions of hexabromide of melting point 177° C.

			Per cent
Baltic .	.	.	57·96
Dutch .			51 73
Argentine		.	51 66
Indian .			50 50

The **thermal reactions** which linseed oil gives are not characteristic enough for purposes of identification, and on account of their indefiniteness and the trouble involved in the determination, their employment is not recommended for isolated tests in an analytical laboratory. For special purposes, however, as in a works where a large number of tests must be made rapidly, the *Maumené* reaction, or, better still, the bromine thermal test, may be usefully applied.

Thus oils that are known to be pure can be quickly sorted into those which have the lowest iodine value, and hence are suitable for soap-making purposes, and those of a high iodine value which are preferably used in the manufacture of varnish and linoleum. It should, however, be understood that the operator himself must determine by experiments the factor which applies to the particular conditions under which the test is carried out. The following table will show how necessary it is for each operator to ascertain the factor which represents, as it were, the personal equation of his experiments :—

Kind of Linseed Oil	Bromine Thermal Value °C I	Hubl Iodine Value.	I×5·5	I: 5·7	I×6·0	Observer.
...	30·1	160·7	167·2		.	Hehner and Mitchell
..	31·3	151·9	172·0	...		,, ,,
Raw linseed .	30·55	171·3	.	173·9		Jenkins[1]
Old sample .	28·5	167·1	.	·	171·0	,,
..	28·8	177·0	.		172·8	Archbutt[2]
American (?)	29·6	177·0			177·6	,,
.	29·7	177·8			178·2	,,
East Indian .	29·8	178·7	.	.	178·8	,,
,, ,,	30·45	183·3	...	..	182·7	,,
Baltic . .	31·35	188·5	..	..	188·1	,,
,, . .	31·4	188·8	...		188·4	,,
,, . .	31·75	188·8	...		190·5	,,
,, . .	32·5	192·5	..	..	195·0	,,

In doubtful cases the determination of the iodine value must of course be resorted to, as only this test furnishes unmistakable results.

Oxygen Absorption.—The rapidity with which a given sample of linseed oil dries, and the amount of oxygen it absorbs, afford guidance in the valuation of a linseed oil recognised as pure ; for the commercial value of a sample of linseed oil intended for the manufacture of varnish depends on its drying power, which is determined by the amount of oxygen it absorbs, and also by the time it requires for drying to an elastic skin. The *Livache* method, as also the glass-plate method, may be applied for quantitative purposes (cp. Vol. 1. Chap. VII.), but except in special cases little information can be derived therefrom.[3] It is of far greater importance to observe the time required to dry, and the nature of the skin formed. This test is the one usually applied in technical work. It requires, however, a good deal of practical experience to judge of the quality of an oil by the drying test. The analyst called upon to give an opinion should compare a given sample with an oil known to be pure and of good quality, by exposing side by side a number of glass plates coated, by means of a palette knife, with a very thin film of oil, so that exactly the same conditions obtain throughout. A good linseed oil should become dry in less than three days ; it should not be tacky on touching with the fingers, and should yield an elastic, coherent skin. Oils containing considerable amounts of unsaponifiable matter or foreign oils will be incidentally detected by this test, inasmuch as these prevent the formation of a good elastic skin. Linseed oil mixed with 5 per cent pyridine is stated to dry slowly and uniformly without cracks.[4]

An important test in judging of the suitability of a linseed oil for making paint oils and varnishes is to heat a few c.c. in a test-tube up

[1] *Journ. Soc. Chem. Ind.*, 1897, 194.   [2] *Ibid.*, 1897, 311.
[3] For a modification of Livache's tests cp. Elsdon and Hawley, *Analyst*, 1913, 1.
[4] W. Ostwald. English patent 10,361, 1910.

to 600° F., that is, until the oil commences to boil up. Good oil should remain clear on cooling (as a rule it will have become lighter in colour). From impure oils mucilaginous matter ("foots," see p. 57) will separate as a gelatinous mass at the bottom of the test-tube , in the case of low quality oils this mass will be found disseminated through the oil. Oils of this kind are unsuitable for the manufacture of paint and varnish oils (cp. also Chap. XV. B. iii. and iv.).

Linseed oil, being one of the cheapest fatty oils, is not frequently adulterated with vegetable oils. However, when the price of linseed oil is high, cheaper oils are extensively added as adulterants.

Drying Oils.—The presence of considerable quantities of drying oils, such as candle nut oil, safflower oil, sunflower oil, and especially soya bean oil, is indicated by an iodine value lower than 175. Their presence would also be indicated by the bromide test, if the yield of the ether-insoluble bromides of the mixed acids falls below 30 per cent. Since tung oil and poppy seed oil yield no ether-insoluble bromides, safflower, soya bean, and walnut oils a very small quantity only, and candle nut oil less than half of the quantity to be expected from linseed oil, the bromide test will be found of greater help than the iodine test.

Cotton Seed Oil.—An inducement to adulterate linseed oil with cotton seed oil will only present itself whenever the latter is cheaper than linseed oil. The presence of cotton seed oil would be detected by a low iodine value of the sample. The *Halphen* colour test should be applied as a confirmatory test (see p 203) ; the melting point of the fatty acids should also be determined. In the presence of considerable quantities of cotton seed oil, the titer test number will be considerably above 20° C.

Rape oil is indicated by a lower saponification value than the normal one (of course, in the absence of unsaponifiable oils). A few per cent of rape oil, such as are frequently present in commercial linseed oil, will not be detected thereby. The saponification value will, however, in many cases afford some guidance as to the excess of foreign seeds in the linseed from which the sample has been obtained. In important cases the determination of erucic acid (Vol. I. Chap. VIII. p. 553) must be carried out.

Fish Oils—Blubber Oils.—Since fish oils absorb fully as much iodine as linseed oil does, and yield as much and even more ether-insoluble bromides, the quantitative tests alone will give a satisfactory answer, and it is imperative to take the melting point of the ether-insoluble bromide of the mixed fatty acids. In the case of pure linseed oil, a white or only slightly yellowish hexabromide is obtained, melting sharply without decomposition at 175°-180° C., whereas the octobromides from fish and blubber oils become dark or almost black at 200° C., and do not melt. Even 10 per cent of fish oil can thus be detected. In doubtful cases the phytosteryl acetate test will furnish a reliable means for the detection of fish (liver) and blubber oils. Crystallised phyto-steryl acetate from pure linseed oil melts at 128°-129° C. (*Bömer and*

Winter).   In the presence of cholesterol the melting point of the acetate
is much lower.

Unsaponifiable Matter.—Adulteration with mineral oils and rosin
oils is still practised, although these oils are very easily detected.   If
only one of these two oils be the adulterant, the specific gravity of the
sample alone will indicate the further line of examination.   A judiciously
prepared mixture of both unsaponifiable oils will, however, have the
proper specific gravity of linseed oil.

The presence of either adulterant is readily indicated by a low
saponification value (below 190) ; the amount of the adulterant is
determined by weighing the unsaponifiable matter.   Pure linseed oils
contain no more than 1-2 per cent of unsaponifiable matter.   If a
notable amount of unsaponifiable matter has been found, and the
presence of rosin oil be suspected, polarimetric examination will give
useful indications.   Linseed oil is practically optically inactive—a
sample of East India oil, examined in a 200 mm. tube, showed the
deviation of $0°$ $6'$ to the right—whereas rosin oil is strongly dextro-
rotatory (cp. Vol. III. " Lubricating Oils ").

Rosin (colophony) is best detected qualitatively by applying the
Liebermann-Storch reaction.   If the colour of the sample be very dark,
it is best to warm it with alcohol, so as to extract the bulk of the colo-
phony, and test the alcoholic extract.   The amount of rosin can be
determined quantitatively by titrating the sample with aqueous
standardised alkali, using phenolphthalein as an indicator.   From
the amount so found, there must be subtracted the amount of alkali
used for neutralising the free fatty acid in linseed oil—which rarely
exceeds about 3 per cent.   Test experiments made in my laboratory
with mixtures of linseed oil and rosin proved the reliability of this
method.   If, however, a large amount of linseed oil fatty acids is present,
as in linseed oil soap stock (see Vol. III.), the amount of rosin in the
alcoholic extract must be determined quantitatively by *Twitchell's*
method.

Linseed oil is very extensively used as stock material for soft soaps :
for this purpose those oils are especially employed which have com-
paratively low iodine values.   The presence of mucilage in linseed oil
is, as a rule, not objected to by the soapmaker.   The most important
application of linseed oil is found in the manufacture of boiled oil for
paints, varnishes, lithographic varnishes, and for the manufacture of
linoleum.   No other drying oil approaches the properties of linseed oil,
the drying oil *par excellence*.   Hence linseed oil is also the best oil for
making putty.   The preparation of plastic masses by heating linseed
with finely divided magnesium or iron (reduced by means of hydrogen)
has been patented by Meusel & Co.[1]

The manufacture of **boiled oil**, its characteristics, and detection
if in admixture with linseed oil, will be treated in Chapter XV., as
also the chemistry and technology of oxidised linseed oil.

Linseed oil is also used in the manufacture of " Vulcanised Oils "

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[1] German patent 202,510 (Chemische Fabrik Liegnitz, Meusel & Co., cp. Vol. III.
Chap. XV. " Polymerised Oils ").

(cp. Vol. III. Chap. XV.), and for extracting india-rubber from " waste rubber."

By heating linseed oil with sulphur, the official *oleum lini sulf.* is prepared.

Linseed oil fatty acids are now produced as a commercial article. by autoclaving linseed oil. The commercial product, " linseed oil soap stock fatty acids," consists as a rule of from 80 to 85 per cent of free fatty acids, the remainder being unsaponified fat The " fatty acids " are chiefly used in the manufacture of soft soap. They are also employed as solvents in the production of " fat-soluble " colours.

Smaller quantities are also employed in the industry of spirit lacquers, it being claimed for them that they assist the drying of the lacquers.

N'GART OIL

N'Gart oil[1] is obtained from the fruits of *Plukenetia conophora*, Mull. Arg., a liana belonging to the family *Burseraceæ*, widely cultivated in the Cameroons (district Ossidinge) between the maize plant. The fruit, of the size of a walnut, contains a nut having a thin shell, which encloses a loose round kernel. The weight of a kernel varies from 4 to 5 grms ; it contains 53·8 to 59 per cent of a pale yellow oil.

The following characteristics were ascertained :—

Specific gravity at 15° C .	. .	0 9360
„ „ 17 5° C	.	0 9354
Solidifying point .	− 33° C.	− 16 to − 20° C.
Saponification value	.	192
Iodine value .		177·3 ; 204[2]
Refractive index at 17·5 C. .	.	1·4830
„ „ 15° C. .	.	1·4835
Iodine value of the mixed fatty acids	.	187·4 ; 190·210

A specimen examined by *Muhle and Hammelmann*[3] contained 3·01 per cent " oxidised acids," and yielded 47·7 per cent of ether insoluble bromides melting at 177-178° C. The fatty acids had an iodine value of 211. On heating for six hours at 300° the oil gelatinises in a similar manner to Chinese wood oil.

The fruits are gathered by the natives, and the expressed oil used for edible purposes. The taste of the oil is similar to that of linseed oil. Its high iodine value also points to its use as a substitute for linseed oil. Attention has been drawn to this oil whilst the prices of linseed oil were abnormally high.

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[1] Native name.—Brieger and Krause, *Zeitschr. f. angew. Chem.*, 1909, 1373 ; M. Krause and Diesselhorst, *Tropenpflanzer*, 1909, xiii. 281 ; *Chem. Rev.*, 1912, 138 ; D. Holde and G. Meyerheim, *Chem. Zeit.*, 1912, 1075.

[2] By Wijs' method.

[3] *Chem. Zentralbl.*, 1913, 1. 587.

TUNG OIL

Under the name " Tung Oil " are comprised here two fatty oils, which are differentiated in commerce, according to their origin, as " Chinese Tung Oil " and " Japanese Tung Oil." Synonymous are the terms " Chinese Wood Oil " and " Japanese Wood Oil." Both oils are sold in commerce as " Wood Oil," but this term should be avoided in order to exclude confusion with the ethereal gurjun oil (*gurjun balsam*), also known in commerce as *wood oil*. As the two kinds of tung oil differ somewhat, especially in their specific gravity, the characteristics of the two oils will be given separately.

(*a*) CHINESE TUNG OIL (CHINA WOOD OIL)

French—*Huile d'abrasin, Huile de bois de Chine.* German—*Chine-sisches Tungöl, Chinesisches Ölfirnisbaumöl (Chinesisches Holzöl).* Italian—*Olio di legno del China.*

For tables of characteristics see pp. 75, 76.

Chinese tung oil (first mentioned by the Jesuit D'Incarville (about the year 1735) as a common adulterant of Chinese lacquer) is obtained from the seeds of *Aleurites cordata*, Müll. Arg. (*Elæococca cordata*, Bl. , *Elæococca vernicia*, Juss. ; *E. sinensis, Dryandra vernica*, Carr.), a tree indigenous to China [1] (Chinese, *Tung Yu*). Trees belonging to the same species also grow abundantly in Indo-China, Tonkin, Annam, and Cambodja (Tonkinese, *Cây-tràou* ; Annamese, *Cây-dau-son* ; Cambodjese, *Doeum-chor-tuc*).

The fruits form a nut, in which three to five seeds having a hard shell and an oleaginous kernel are enclosed ; hence in China the oil is frequently termed " nut oil," a name also used frequently in commerce (*e.g.* " China nut oil ").

The composition of Chinese tung oils varies somewhat according to their source, and the treatment of the seeds in different localities. Three kinds of seeds are distinguished—yellow (*pay-yu*), drab (*hsin-yu*), and white (*hung-yu*). The seeds are roasted in a flat dish over a naked fire and then broken to powder between stones ; finally the mass is expressed in crudely made wooden presses. The kernels contain about 53 per cent of oil, but the practical yield of oil amounts to only 40-41 per cent. It has not been profitable to substitute for the native plant modern hydraulic presses (cp. p. 14). The cold-drawn oil is pale yellow, and is termed " white tung oil." This is the variety chiefly imported into Europe. The oil obtained by hot pressing is dark brown, and termed " black tung oil." This oil is consumed at home ; it has an unpleasant taste, and its odour is more pronounced than that of the white tung oil, which is also somewhat unpleasant. (This odour precludes its use for many

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[1] *Paulownia imperialis*, Sieb. et Zucc. (?)

purposes.)   The characteristic smell seems to develop whilst the oil
is in transit to Europe, for oil expressed from fresh seeds on the spot
is stated to have by no means an unpleasant smell.   The objectionable
smell is ascribed [1] to oil originating from damaged kernels.

The cakes are poisonous, and are therefore only used as a fertiliser,
or for the manufacture of lampblack.   Poisonous properties have
also been attributed by some writers to the tung oil itself, but this is
open to doubt.

About one-half of the oil is produced in the provinces Hunan and
Kweichow ; about one-third in Szechuan, and the remainder in
Hupei (mostly in the neighbourhood of Ichang).   Szechuan oil has
the lightest colour.   The oil is made in small quantities by a large
number of producers, from whom it is collected by middlemen, who
bring it to Hankow, where foreign merchants clarify the oil and pack
it for shipment.

Statistics of production are not available, but the extent of the
industry may be gathered from the customs returns stating the
export figures from 1897 (when the first shipments were made to
Europe) up to 1911 :—

Exports of Tung Oil from Hankow and Wuchow

Year	Hankow		Wuchow (Canton)
	To Foreign Countries	To Chinese Ports [2]	
	Tons		Tons
1897	13,049		287 [3]
1898	19,707		653
1899	21,044		1237
1900	19,653		1456
1901	16,701		1802
1906	28,685		..
1907	23,540		
1910	7,955	42,702	.
1911	6,143	37,841	.

The home consumption of China is estimated to be at least double
the amount of oil exported.

The export from French Indo-China has reached 300 to 400 tons
per annum during the last eight years.

The imports of Chinese tung oil into Germany amounted in the
years 1911 and 1912 to 8665 and 6796 tons respectively.

Experiments have been made to grow the China wood tree in
Chico, California.   Although the United States forestry department
has already planted a considerable number of trees, and is ready
to distribute 5000 runners to the members of the Paint Manufacturers

[1] Cp. Fahrion, *Zeitschr f. ang. Chem.*, 1905, 406.   [2] Shanghai, etc.
[3] Seven months only.

Association, it is doubtful whether the cultivation will be attended with success.

Chinese tung oil consists chiefly of the glycerides of oleic and elæomargaric acids (Vol. I. Chap. I.). According to *Fahrion*,[1] tung oil contains 2 to 3 per cent of saturated fatty acids and about 10 per cent of oleic acid. Although tung oil gives in the bromide test 0·38 per cent of a precipitate, its fatty acids do not yield any ether-insoluble bromide, neither by the method described Vol. I. Chap. VIII. p. 570, nor by *Eibner and Muggenthaler's* method, *ibid.* p. 573. In the elaïdin test an oily layer is obtained resting on a lower, nearly solid product ; when stirred up, the whole mass flows.

On keeping, tung oil becomes jellified and solidifies partly. A specimen kept by the author for a number of years with occasional access of light had solidified to gelatinous and jelly-like tough masses which were interspersed with crystals. *Cloez*,[2] who first observed this phenomenon, gave the explanation that the liquid glyceride was converted into an isomeric solid glyceride — eleostearin — which solidified at 32° C. and melted at 34° C. *R. S. Morrell*[3] observed that in Hankow oil, exposed to light in well-stoppered glass bottles, crystals appeared after a short time, and that after one year about 6 per cent of the oil had been converted into the crystalline isomeride. The crystals, isolated by washing with acetone, melted at 61-62° C. The oil obtained from the acetone solution after distilling off the solvent in a current of carbon dioxide yielded in a few days a further crop of crystals after exposure to light. Once the crystallisation had started, treatment with acetone seems to accelerate the transformation on exposure to light. The crystals are soluble in chloroform, ether, and benzene ; they are very sparingly soluble in cold alcohol—even boiling alcohol dissolves about 5 per cent only,—and are readily soluble in hot glacial acetic acid. The crystalline substance is very readily oxidised, and the oxidised glyceride is quite insoluble in warm glacial acetic acid. (Difference from the original oil.)

[1] *Chem. Zeit Rep.*. 1912, 612.
[2] *Compt. rend.*, 1876 (81), 169 , 1877 (82), 501.
[3] *Journ. Chem. Soc* . 1912, 2083 . cp. also Kitt, *Chem. Revue*, 1905, 212

Physical and Chemical Characteristics of Chinese Tung Oil

	Specific Gravity		Solidifying Point.[6]		Saponification Value		Iodine Value		Thermal Tests. Heat of Bromination.		Refractive Index.		
	At °C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At °C.		Observer.
Chinese Tung Oil	15	De Negri and Shurlati	2-3	De Negri and Shurlati			159-161	De Negri and Shurlati					
	15.5 (water at 15.5°C =1)	Lewkowitsch					163.4	Lewkowitsch					
	"	Kreikenbaum[2]			189.8 191.8	Kreikenbaum	169- 173.3	Kreikenbaum[3]					
	"	Chapman			192.0 194.6	Chapman	166.4 156.2	Chapman[10]	23.10- 23.57	Chapman	20	1.5169 1.5207	Chapman
	"	Browne[3]					156- 171	Hoepfner and Burmeister[11]			20	1.5110 1.5202	Hoepfner and Burmester Boughton
Japanese Tung Oil	15.5	Boughton[1] Lewkowitsch Nash			191.4- 193.1	Lewkowitsch Zucker	150.2	Lewkowitsch			15.6	1.5211- 1.239 1.5099 1.5186	L. E. Wise
	"	Chapman[5]			185.18 197 193.4- 193.3	Chapman[5]	149.0- 158.0	Chapman[5]	23.10- 24.70	Chapman[5]	25	1.5034 1.5083	Chapman
	24 (water at 24=1)	Kanetaka			196	Kanetaka	161.3	Kanetaka			25		

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[1] Prepared in the laboratory from seeds, Chem. Zeit, 1890, 275   [2] Journ. Ind. Eng. Chem., 1940, 205.   Samples from ten shipments extending over two years
[3] Chem. News, 1912, 15   [4] Seventh Intern. Cong. Applied Chem. Sec. I p. 89 (1910)   [5] Commercial samples
[6] Expressed oil
[7] Unsaponifiable matter 1.2 and 0.4 per cent.   [8] Unsaponifiable matter 0.7-1.0 per cent
[9] With Hubl's solution 4 to 18 hours With Hanus solution much higher value up to 210 were obtained The same observation has been made by E. W. Boughton
[10] With Wijs solution
[11] Chem. Zeit., 1913, 15

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Acids + Unsaponifiable		Solidifying Point		Melting Point		Neutralisation Value		Iodine Value	
	Per cent	Observer	°C	Observer	°C	Observer	Mgrms KOH	Observer	Per cent	Observer
Chinese Tung Oil	95·0	Boughton	31·2	De Negri and Sburlati[1]	43·8	De Negri and Sburlati[1] Williams	188·8	De Negri and Sburlati	159·4	De Negri and Sburlati[1]
					40				145·0	Lewkowitsch
			Titer Test						Liquid Fatty Acids	
			37·1–37·2	Lewkowitsch					179·7	Lewkowitsch
Japanese Tung Oil			Titer Test							
			33·2	Lewkowitsch	40·3	Nash[2]				

[1] Prepared in the laboratory from seeds.   [2] Private communication.

Freshly expressed tung oil consists almost entirely of neutral glycerides; the samples examined in Europe contained at most up to 6 per cent of free fatty acids, calculated as oleic acid. The amount of unsaponifiable matter in the tested samples did not exceed 0·8 per cent.

The characteristic numbers contained in the two tables, p. 75, p. 76, are contrasted with those of Japanese tung oil (Japanese wood oil). Cp. also the table given p. 84.

Chinese tung oil is readily identified by its strong characteristic smell, which it has not been possible hitherto to remove. Chinese tung oil has the highest specific gravity of any known oil with the exception of castor oil, with which it cannot be easily confounded. (Japanese tung oil has a lower specific gravity, viz. 0·933-0·935 at 15·5° C.)

The oil is readily differentiated from linseed oil by the manner in which it dries. It possesses even more strongly pronounced drying power than linseed oil, in that it forms a skin more rapidly than linseed oil, but it differs from the latter oil in that it gives on a glass plate a dry opaque skin, which is wax-like, but has no elasticity.

Boughton states that in the *Livache* test, using 0·5 grams of oil and 5 grams of litharge, several specimens of tung oil gained after 48 hours from 0·9 to 5·9 per cent, and after 96 hours from 3·6-8·7 per cent of oxygen, whereas samples of linseed oil gained in the same time respectively 12·9 and 13·7 per cent.

The film formed by allowing tung oil to dry on a glass plate consists to a considerable extent of oxidised acids, and is characterised by a low iodine value as also by a notable amount of soluble fatty acids. The product, termed by *Fahrion* "tungoxyn" (cp. "linoxyn," p. 63), will be further described in Vol. III. Chap. XV. under "Linoleum."

At higher temperatures than the ordinary one, tung oil dries more rapidly (*Fahrion*; cp. *Chapman* [1]).

When heated with lead oxide or red lead, the oil gelatinises within fifteen minutes to a light brown mass.

A very characteristic property of the earliest specimens of tung oil imported in Europe and examined by the author was to form a jelly on being heated to 250° C. for a short time, or even when kept at 180° C. for an hour or two. The jelly-like mass so obtained possesses some elasticity, is insoluble in the ordinary solvents of oil, and shows no tendency to melt on being again heated to 280° C. The specimens imported during the latter years require higher temperatures for gelatinisation—viz. 280° C. and even 310° C., if only about ten minutes' heating be allowed.[2] The gelatinisation is not due to oxygen absorption, as has been assumed by some observers, since the conversion into a semi-solid mass takes place when air is carefully excluded. Further study of the properties of elæomargaric acid,

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[1] *Analyst*, 1912, 549.
[2] Oil extracted with petroleum ether polymerises less rapidly than expressed oil (*Chapman*). De Negri and Sburlati had also observed that oil extracted with carbon bisulphide behaves differently from expressed oil.

which distinctly differs from linolic acid, may lead to a proper explanation of the curious behaviour of this oil on heating. The change is very likely due to polymerisation of the glycerides (cp. Vol. III. Chap. XV. B ii. (2) " Polymerised Tung Oil "), and must not be confounded with the change which the oil undergoes in insolation.

H. Wolff [1] states that the gelatinised product obtained by heating Chinese wood oil is not a homogeneous product, but a colloidal solution of polymerised oil in unchanged oil, which latter can be extracted by ether, chloroform, or benzene. The insoluble portion is stated to be capable of gelatinising considerable quantities of tung oil or linseed oil on heating. The insoluble portion yields after treatment with dilute sodium carbonate, a liquid fatty acid of the iodine value 11·5-19 8, and neutralisation value 352-398 ; whereas the fatty acids from the portion not attacked by cold sodium carbonate solution had the iodine value 82-106, and neutralisation value 128-147.

The behaviour of Japanese tung (wood) oil on heating is contrasted with that of Chinese tung oil, p. 84.

Several methods have been patented to prevent coagulation of tung oil on heating. Thus *A. Weinschenk* [2] suggests heating the oil with 0·01 to 0·02 per cent of zinc dust to 80-90° C. The *Société Anonyme " Vernisol "* [3] protects the addition of naphthenic acids. *A. Beringer* [4] claims the addition of sulphur, sulphides, selenium, selenides, or mixtures thereof.

If a saturated solution of iodine in chloroform or any other solvent be dropped on tung oil, the oil is immediately solidified ; and if the oil has been previously dissolved in chloroform, a jelly is obtained (*Jenkins*). Bromine has no such action on the oil.

P. C. McIlhiney [5] suggested to determine the proportion of tung oil in admixture with other oils by treating a solution of the oil in glacial acetic acid with iodine, and removing the undissolved portion by washing with low boiling petroleum ether. This method has not yet been worked out to a quantitative one.

Concentrated sulphuric acid gives a black clot with the oil. When 1 grm. of the oil is dissolved in 5 c.c. of chloroform, and 5 c.c. of a saturated solution of iodine in chloroform is added, and the mixture stirred, the whole is converted into a stiff jelly after about two minutes. If 2 grms. of the oil be employed under the same conditions, the jelly is so stiff that it can be granulated.

Sulphuric acid of specific gravity 1·597 to 1·759 is also capable of effecting the polymerisation of tung oil. The most suitable sulphuric acid for this purpose is stated to be that of the specific gravity 1·688 (cp. also " Polymerised Tung Oil," Vol. III. Chap. XV.).

In *Redwood's* viscosimeter, 50 c.c. of the oil required 1433 seconds as compared with 28 seconds for water. A further number of viscosimetric observations is contained in the table due to *Chapman* (see below, p. 83).

[1] *Farben-Zeit.*, 1913, 1171.   [2] German patent 219,715.
[3] German patent 253,845.   [4] German patent 261,403.
          [5] *Journ. Ind. Eng. Chem.*, 1912.

In *Valenta's test* the temperature of turbidity is 44°-47° C.

In the *sulphur chloride test* 5 grms. of the oil treated in the cold with 2 c.c. of sulphur chloride and 2 c.c. of carbon bisulphide give in 1½ minutes a thick, stiff jelly.

The *refractive index* of tung oil is much higher than that of any known fatty oil. It should be noted that it cannot be examined in the butyro-refractometer, since its high refraction would place the critical line beyond the 100 degree limit of this instrument (as in the case of rosin oils, see Vol. I. Chap. V.).

Tung oil, on account of its drying properties, suggests itself as a substitute for linseed oil, but although it is the most rapidly drying oil known hitherto, it cannot replace linseed oil in the industry of paints, varnishes, linoleum, etc. About ten years ago, when tung oil was shipped in large quantities to Europe, and was therefore somewhat strongly pressed on the market, a large number of patents were taken out purporting to put tung oil to the same uses as linseed oil, or at least to employ it in admixture with linseed oil.

During the last few years, when the price of linseed oil was abnormally high, more extensive use has been made in the arts of Chinese tung oil as a substitute for linseed oil. In the United States endeavours have even been made to replace linseed oil completely by Chinese tung oil. In consequence of these endeavours not only were the most extravagant claims made for the properties of tung oil, but the oil itself, having attained high prices, has become adulterated to a considerable extent.

Earlier statements that tung oil was adulterated with cotton seed oil have not been borne out by examinations carried out by the author. Recently, however, adulteration with stillingia oil, soya bean oil, and sesamé oil has been practised to a considerable extent. The *specific gravity* and *refractive index tests* are the most important ones to be used in the examination of suspected samples. Sesamé oil is readily detected by the *Baudouin* test. Stillingia oil might probably be detected by the optical rotation of the sample, as Chinese tung oil is practically optically inactive (*Chapman*). Small quantities of soya bean oil are, however, very difficult to detect; as they cannot be revealed with certainty by the iodine absorption test.[1] Hence recourse has been taken to the *gelatinisation test* as a supplementary means for revealing the addition of small quantities of soya bean oil and stillingia oil.

Thus the New York Produce Exchange (on the recommendation of the Committee on Vegetable Oils and Fats) adopted the following rules as determining the basis of character and quality for Chinese tung oil :—

Prime Chinese oil shall be pale in colour (according to season's production), merchantably free from foots, dirt, and moisture; the total impurities not to exceed 1 per cent; impurities not plainly adulterations, up to 5 per cent, shall not justify rejection; but allowance to be

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[1] Curiously enough, whereas the Wijs and Hübl solutions give almost identical results, the Hanus solution gives much higher values. This must be due to the constitution of the tung oil fatty acids, inasmuch as linseed oil under the same conditions does not give such widely different results with the Hanus solution (cp. Vol. I. Chap. VI.).

made by sellers for such impurities in excess of 1 per cent. Prime oils shall show with a Tagliabue viscosimeter at a temperature of 70° F. from 7·25 upward. The oil to satisfy the requirements of either the *Bacon* test, or the *Worstall* test.

Bacon's Test.—In four test-tubes of $\frac{3}{4}$ inch diameter and 4 inches in length are placed :—(1) 10 c.c. of pure tung oil; (2) 10 c.c. of the same tung oil containing 5 per cent of a vegetable oil ;[1] (3) 10 c.c. of tung oil containing 10 per cent;[1] (4) 10 c.c. of the sample to be tested. The four tubes are immersed in an oil bath having a temperature of 288° C.

The tubes are maintained at a temperature from 280° to 285° C. (maximum) for exactly 9 minutes ; the tubes are then withdrawn and the sample compared with the contents of the first three test-tubes. Each tube is stabbed from top to bottom with a small bright spatula. Pure oil gives a hard clean cut, and when the knife is withdrawn the incision looks like a straight line, while an oil having as little as 5 per cent of an adulterant will invariably be softer, and the incision will have a peculiar feathered effect ; an oil containing 10 per cent of an adulterant will be soft, while the presence of an adulterant exceeding 12 per cent will cause the oil to remain entirely liquid.

Worstall's Test.—One hundred grms. of the oil are heated in an open metal pan, 6 inches in diameter, as rapidly as possible, to a temperature of 540° F. The time required to heat the oil from room temperature to 540° should be, as nearly as possible, the same each time, four minutes being sufficient with gas burners. The oil is kept at or as near to 540° as possible, stirring until it starts to solidify. The time required after the oil reached 540°, until it started to solidify, should not exceed $7\frac{1}{2}$ minutes for pure oil. When the oil has solidified in the pan, it is turned out while still hot, and cut with a knife. Pure oil gives a product that is pale, firm, and cuts under the knife like dry bread, not sticking. If the oil requires more than $7\frac{1}{2}$ minutes after reaching 540° until starting to solidify, or if the product is dark, soft or sticky, the oil should be rejected.

L. S. Potsdamer[2] rejects this test as unsatisfactory, and proposes to determine the temperature of polymerisation, which in the case of pure oils is about 289° C., but said to be considerably lower for oils adulterated with soya bean oil or mineral oil.

Chapman, who also rejects these tests as unsatisfactory, suggests in place thereof the following method as yielding definite and concordant results :—

Two test-tubes 6 inches long by $\frac{5}{8}$ inch diameter, containing about 5 c.c. of the oil to be examined, are immersed in a bath of melted paraffin wax at a temperature of about 100° C. ; the temperature of the bath is then raised to 250° C. within about fifteen minutes. The time is then noted, and the temperature of the bath maintained constant at 250° C. After half an hour one of the tubes is withdrawn, allowed to cool, and, when cold, is broken, and the jelly examined. The other tube is kept

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[1] No special oil is mentioned ; soya bean oil or sesamé oil would be the most suitable oils.

[2] *Eighth International Congress Appl. Chemistry*, vol. xxv. 791.

in the bath at 250° C. for a further period of half an hour, when it also is withdrawn, allowed to cool, and then broken. Chinese tung oil of good quality should give after half an hour a fairly firm jelly, which after another half-hour's heating should be quite hard. Comparative tests must of course be made with samples known to be pure.[1]

In the following table containing the results of the examination of seventeen samples of tung oil from Hankow, the terms "very hard," "hard," and "fairly hard" denote the consistence of the polymerised oil. When cut with a knife or broken across, the cut or fractured surface should be smooth and free from stickiness, and small portions when rubbed in the hand should break down completely into a soft crumbly mass, which should not adhere to the fingers.

Sample	Specific Gravity, 15°/15° C	Saponification Value	Iodine Value	Refractive Index at 20° C	Time of Efflux at 15.5° C Seconds	Polymerisation Test One Hour at 250° C
1	0·9419	196·6	169·9	1·5207	2178	Very hard
2	0·9406	193·8	168·4	1·5181	1636	Hard
3	0·9426	194·3	166·5	1·5190	1946	Fairly hard
4	0·9417	193·0	166·4	1·5170	1880	,,
5	0·9430	195·6	168·8	1·5195	2017	Very hard
6	0·9440	194·5	170·0	1·5180	1849	Hard
7	0·9416	193·0	168·6	1·5150		Fairly hard
8	0·9414	192·0	171·0	1·5170		Hard
9	0·9437	194·1	169·7	1·5176	1997	,,
10	0·9420	192·5	173·0	1·5165	1722	,,
11	0·9417	192·0	176·2	1·5168	1605	,,
12	0·9429	196·0	172·6	1·5180	1740	,,
13	0·9427	194·6	174·2	1·5182	1690	,,
14	0·9430	195·0	173·7	1·5194	1820	,,
15	0·9440	194·6	172·8	1·5193	2047	,,
16	0·9420	195·2	169·5	1·5160	1804	,,
17	0·9433	195·2	169·6	1·5187	1820	Very hard

Hoepfner and Burmeister[2] obtained the following results with *Bacon's* test : —

Sample	Iodine Value	Refractive Index at 20° C	Bacon's Test		
			Heated to ° C	Minutes	Consistence
1	171	1·5195	280	9	Solid
2	170	1·5178	280	9	Sticky
			310	12	Solid
3	168	1·5193	280	9	Solid
4	163	1·5197	280	9	Solid
5	164	1·5202	280	9	Sticky
			310	12	Solid
6	158	1·5149	280	9	Liquid
			310	12	Solid
7	159	1·5188	280	9	Solid
8	158	1·5155	280	9	Solid
9	162	1·5155	280	9	Solid

[1] Cp. also F. Browne. *Chem. News*, 1912, 14.   [2] *Chem. Zeit.*, 1913, 39.

Hoepfner and Burmeister conclude that the *Bacon* test should be modified by heating the samples to 310° C. for 12 minutes. Genuine oil should, after cooling to the ordinary temperature, be so hard that it can be broken up in a mortar to a coarse powder.

In China tung oil is used chiefly as a natural varnish for wood, for caulking junks and boats, as a common adulterant of lacquer, and also for lighting. Large quantities are also consumed for waterproofing paper and all kinds of tissues. The oil is further employed in admixture with powdered lime as a mortar. The best kinds of Chinese ink are obtained by burning the oil with a regulated amount of air. The cold-drawn oil is stated to be used in medicine as an emetic and also as a purgative. (According to *Hertkorn*[1] tung oil is poisonous.)

Further information on the technical applications of tung oil in the paint and varnish industries will be given in Vol. III. Chap. XV. under " Polymerised Oils " and " Oxidised Oils," and " Linoleum Substitutes."

Tung oil fatty acids became a commercial article at the time when linseed oil fatty acids had reached abnormally high prices. Like the latter they have been recommended as a substitute for shellac in the manufacture of spirit lacquers, it being claimed that they assist the drying of the lacquers, and that on account of their property of drying to a dull skin, they are capable of giving the lacquer the special dull surface which is desired in some special cases.

Intermixed with *Aleurites cordata* there occurs in the Chinese province Fokien *Aleurites Fordii*, Heussl., the seeds of which also furnish commercial tung oil ; and it appears that the Chinese tung oil is indiscriminately prepared from the seeds of *Aleurites cordata* or *Aleurites Fordii*, or mixtures of the two.

The nuts of *Aleurites Fordii* are known under the name " kaloo nuts " ; they are poisonous. The oil extracted from the seeds of *Aleurites Fordii* differs very little from the oil from *Aleurites cordata*. The examination of the tung oil from *Aleurites Fordii* carried out in the Imperial Institute[2] furnished the following characteristics :—

Specific gravity at 15° C.	0·9404
Saponification value	191·8
Iodine value	166·7
Insoluble fatty acids	94 6 per cent
Titer test	42·42·5° C.
Acid value	2 89

(b) JAPANESE TUNG OIL (JAPANESE WOOD OIL)

French—*Huile de bois du Japon.* German—*Japanisches Tungol, Japanisches Ölfirnisbaumol (Japanisches Holzol).* Italian—*Olio di legno del Giappone.*

Japanese tung oil is obtained from the fruits of *Elæococca vernicia*,[3] which grows in the southern provinces of Japan (Echizen and Wakasa),

[1] *Chem. Zeit.*, 1903, 635.
[2] *Bull. Imp. Inst.*, 1907, 134 ; cp. also Chapman, *Analyst*, 1912, 549.
[3] Kametaka, *Journ. Coll. Science Imp. Univ. Tokyo*, 1908.

and especially in the island of Yeso (Hokkaido).   The Japanese name
of the tree is "*Abura Kiri, Jani Kiri.*" This name has given rise
to confusion with the true Japanese " kiri " tree (" Kirinoki "), viz.
Paulownia imperialis, Sieb. et Zucc. (*Bignonia tomentosa*, Thunb.),
the oil from which, though apparently similar in some of its character-
istics to Japanese tung oil, must not be confounded with the latter.[1]
  The characteristics of Japanese tung oil are contrasted in the tables,
pp. 75, 76, with those of Chinese tung oil.   The characters of a few com-
mercial oils examined by *Chapman* are set out in the following table :—

Oil from	Specific Gravity, 15°/15° C.	Saponifica- tion Value	Iodine Value.	Refractive Index at 20° C.	Time of Efflux at 15.5° C. Seconds.
Wakasa . . .	0·9377	195·2	158·0	1·5083	1230
Idzumo . . .	0·9400	193·4	149·0	1·5052	1620
(?) . . .	0·9349	196·3	151·8	1·5034	...

The iodine values given in this table and the table on p. 75 show that
Japanese tung oil has a lower iodine value than Chinese.   It should,
however, be pointed out that a specimen of fresh tung oil (from Echizen)
pressed in the cold had the iodine value 161·3 (*Kametaka*).   After
keeping the oil in an ordinary stoppered bottle for eleven months the
iodine value had fallen to 150°.

The cake obtained in the preparation of tung oil used to be credited
with poisonous properties, and was therefore applied to the land as a
fertiliser, but since the Japanese employ higher temperatures than they
did formerly in expressing the oil, the cake has been found to be non-
poisonous.   Probably the seeds contain a cyanogenetic glucoside and
an enzyme which is rendered innocuous by the elevated temperature.[2]

A fresh oil examined by *Kametaka* had the acid value 3·81.
Kametaka concludes that the seeds of *Elæococca vernicia* contain a fat-
hydrolysing enzyme.

Up to a few years ago Japanese tung oil was not exported.   With
the demand that arose for a substitute of linseed oil in consequence of
the high price of the latter, some Japanese tung oil was shipped to this
country, as also to Germany.   The quantities imported by the latter
country amounted to 12 tons in 1911, and to 15 tons in 1912.   Japanese
tung oil is not as valuable in the arts as is Chinese tung oil.   It chiefly

[1] The oil from the seeds of *Paulownia imperialis* is known in Japan as " Abura toi "
(*i.e.* Toi oil).   A specimen said to be *Paulownia imperialis* examined by Chapman gave
the following characteristics :—

Specific gravity, 15°/15° C.	0·9351
Iodine value	153·5
Saponification value	193·5
Refractive index at 20° C. . .	1·5053
Bromine thermal value, ° C. .	24·5

[2] Cp. Divers, *Journ. Soc. Chem. Ind.*, 1908, 433.

differs from the latter by its lower specific gravity and its lower iodine value. The smell of Japanese oil is not so strongly pronounced as that of Chinese wood oil (*Lewkowitsch*). This may, however, be due to the more careful treatment of the seed.

In the polymerisation test Japanese tung oil does not gelatinise, hence it is not accepted in the trade as replacing Chinese tung oil, which is in consequence now sold as " Hankow " and " Wuchow," tung oil to avoid confusion with Japanese wood oil.

The author [1] made the following comparative polymerisation tests with authenticated samples of Chinese and Japanese tung oil :—

	Japanese Tung Oil.	Chinese Tung Oil.	
		No 1	No 2
Original oil	0·93386	0 9412	0·9419
Heated rapidly in wide-mouthed flask to 213° C. (420° F.) . .	0 9349	0·9428	0 9432
„ to 232° C. (450° F.) . .	0·9355	0 9445	0·9411
„ to 250° C. (482° F.) . .	0 9477	0 9448	0·9504
„ to 300° C. (572° F.) .	...	0 9592	solidified to a hard jelly
„ to 310° C. (590° F.) . .	0 9553	0 9638	...
„ to 320° C. (608° F.) .	0 9650	0·9700	.
„ to 330° C. (626° F.) . .	0 9694	solidified to a jelly	
„ to 340° C. (644° F.) . .	0 9760	...	..
Heated to 150° C., and kept there for 2 hours	solidified to a soft jelly	0 9365	...
	0 9477	0·9363	0 9463

It will be gathered that the Japanese oil became polymerised, as is indicated by the higher specific gravity, but did not solidify to as hard a jelly as did the Chinese oils.

The specimens examined by Chapman behaved differently from Chinese wood oil, in that they did not gelatinise but only became " soft " and " very soft."

As stated already, most of the Japanese tung oil is consumed at home, and is used for similar purposes as China tung oil, for caulking junks and boats. But even in Japan itself the tung oil has not been able to oust linseed oil from the market except for some common purposes, such as paper umbrellas.

[1] Unpublished experiments.

LALLEMANTIA OIL [1]

French—*Huile de Lallemantia.*   German—*Lallemantia Öl.*
Italian—*Olio di lallemanzia.*

Physical and Chemical Characteristics of Lallemantia Oil

Specific Gravity at 20° C.	Solidifying Point.	Saponification Value	Iodine Value.	Reichert Value
0 9336	35° C.	185	162 1	1·55

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable	Solidifying Point	Melting Point.	Iodine Value
Per cent. 93·3	11° C.	22 2° C.	166

Lallemantia oil is obtained from the seeds of *Lallemantia iberica*, Fisch. et Mey., a plant belonging to the *Labiatæ*, growing wild in the Caucasus, and cultivated in Russia (near Kieff). *L. Royleana* [2] grows wild in the steppes of Turkestan.

The oil belongs to the best drying oils, as is indicated by its iodine value. A sample of the oil spread on a watch-glass dried after 9 days to a thick, resin-like skin. If the oil is heated to 150° C. for 3 hours, complete drying takes place after 24 hours. The absorption of oxygen, determined by *Livache's* method (using copper powder), was 15·8 per cent after 24 hours for the oil, and 14 per cent after 8 days for the mixed fatty acids. 10 grms. of oil at 18° C. mixed with 2 grms. of concentrated sulphuric acid gave a *Maumené* test of 120° C.

In the elaïdin test 10 grms. of the oil, shaken with 5 grms. of nitric acid, specific gravity 1·4, and 1 grm. of mercury, give after three minutes a dark-red, dough-like mass.

Lallemantia oil is used in Persia, Syria, and Kurdistan as an edible oil and also as a burning oil. It may find technical application as a substitute for linseed oil in the preparation of varnishes.

[1] Richter, *Zeitschr. f. chem. Ind.*, 1887, 230.   [2] *Chem. Zeit.*, 1905, 556.

CANDLE NUT OIL

French—*Huile de bancoulier*,[1] *Huile de noix de Bancoul, Huile de noix de chandelle.* German—*Candlenussol (Kandelnussol), Bankulnussol.* Italian—*Olio di noci di Bankoul.*

For tables of characteristics see p. 87.

Candle nut oil is obtained from the seeds of *Aleurites moluccana,* Willd., a tree widely distributed over the tropics; thus it is found in most of the islands of the Pacific, in the West Indies, Florida, and Brazil. Probably about 15,000 acres in Hawaii are covered with the trees. The fruits resemble ordinary walnuts (" Kukui nuts ") in their appearance; their shell is, however, far thicker. The shell is removed by the natives in a primitive fashion by drying the nuts on hot stones, so that the shell can be readily broken by a slight blow with a hammer. According to some writers the ripe seeds are said to be injurious, whereas in the unripe state they are said to form a wholesome food-stuff of the natives. Seeds (obtained through a reliable source from the South Sea Islands) examined in my laboratory [2] contained 62·25 per cent of oil.

Practically identical numbers with those contained in the table of characteristics were obtained by *Kassler* [3] from Fiji candle nuts, the seeds of which contained 58·6 per cent of oil. The oil cakes obtained on a large scale by expressing the oil from the crushed nuts had the following composition (*Lewkowitsch*) :—

						Per cent
Oil	.	.	.	.	.	8·80
Moisture .	.	.	.	.	.	10 00
Ash	.	.	.	.	.	8 28
Albuminoids	.	.	.	.	.	46·16
Cellulose .	.	.	.	.	.	1·47
Carbohydrates (by difference)				.	.	25·29

The ash contained 23·52 per cent potassium oxide, and 53·04 per cent phosphorus pentoxide.

The cold-drawn oil is limpid, colourless, or yellowish, has a pleasant odour and bland taste, but cannot be used for edible purposes on account of its purging properties.

Although the seeds were examined several months after arrival, the extracted oil contained only 4 per cent free fatty acids. Its acetyl value was 9·86, and the proportion of oxidised acids 0·21 per cent.

[1] *Elæococca vernicia* (see pp. 72, 82) is also termed "faux bancoulier."
[2] *Chem. Revue,* 1901, 156.
[3] *Augsburger Seifensieder Zeitung,* 1902, 689.

Physical and Chemical Characteristics of Candle Nut Oil

Specific Gravity		Melting Point.		Saponification Value.		Iodine Value.		Refractive Index.		
									Butyro-refractometer.	
At °C.	Observer.	°C.	Observer.	Mgrms KOH	Observer.	Per cent.	Observer.	At °C.	"Degrees."	Observer.
15	0.929 0.926	Liquid at −18°	De Negri	192.62	Lewkowitsch	163.7	Lewkowitsch	20	78.5	Lewkowitsch
15.5	0.9265							25	76.0	"
	De Negri Lewkowitsch									

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value Liquid Fatty Acids.	
Per cent	Observer	°C	Observer.	°C	Observer	Per cent	Observer.
95.5	Lewkowitsch	13	De Negri	20-21	De Negri	185.7	Lewkowitsch

The high iodine value places the oil prominently amongst the drying oils. However, the older statements that this oil surpasses linseed oil in drying properties must be considered as erroneous ; not only is its iodine value lower than that of linseed oil, but the proportion of ether-insoluble bromides is much smaller. Thus *Walker and Warburton* [1] ascertained in the author's laboratory that the oil yields from 7·28 to 8·21 per cent of ether-insoluble brominated glycerides, whilst the fatty acids yielded from 11·23 to 12·63 per cent ether-insoluble brominated acids.

Candle nut oil is obtainable in enormous quantities. It is used in its home as a burning oil. It should prove suitable for soap-making, especially for the manufacture of soft soaps. It may also find application in the manufacture of paint oils and varnishes as a substitute for linseed oil. When the price of linseed oil is high, adulteration with candle nut oil may occur. Its presence would be revealed by a somewhat low iodine value of the sample, and a low yield of ether-insoluble bromides. Smaller quantities than 20 per cent could not, however, be detected by chemical means. In doubtful cases practical drying tests must be resorted to.

This oil is also expressed in Madagascar, where the oil is known under the name " Bakoly oil." This name is doubtless a corruption of banconlier (*Aleurites moluccana*).

The kernels of the seeds of *Aleurites moluccana* from the Cameroons contain 6·3 per cent of water and 64·4 per cent of oil (*Fendler* [2]). The oil obtained by extraction with ether has a yellow colour and an acrid smell. Its specific gravity at 15° C. is 0·9254 ; solidifying point, −15° C. ; saponification value, 194·8 ; iodine value, 114·2 ; and Reichert-Meissl value, 1·2. The solidifying point of the fatty acids is 15·5° C., and their melting point 18° C.

On comparing these numbers with those given for candle nut oil (p. 87), it will be observed that the iodine value is considerably lower. This is all the more surprising as *Fendler* states that the oil dries quickly when spread in a thin layer.

Oil obtained from the nuts (" Kirimi nuts ") of *Aleurites triloba*, Forst., is known in India under the name of " Kekuna oil " [3] (candle nut oil).

Aleurites triloba forms one of the best shade trees in Hong-Kong, where it grows very quickly. The roasted nut forms an agreeable fruit.

Seeds obtained in 1907 yielded on examination in the Imperial Institute [4] 60 to 80 per cent of oil, equivalent to a yield of 19·8 per cent from the unshelled seeds. Specimens of nuts examined in the Imperial Institute in 1912 consisted of 64 per cent of shells and 36 per cent of kernels. The latter contained 68·1 per cent of oil. The following characteristics were ascertained :—

[1] *Analyst*, 1902, 237.
[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1903, 1025.
[3] *Journ. Soc. Chem. Ind.*, 1901, 642.
[4] *Bull. Imp. Inst.*, 1907, 136 ; 1912, 44.

	1907 Specimen.	1912 Specimen.
Specific gravity at 15° C. (water at 15° =1) .	0·9274	0·927
Saponification value	204·2	193·7
Iodine value	139·7	151 0
Reichert-Meissl value . . .	1 98	
Insoluble fatty acids+unsaponifiable .	96·4 per cent	
Titer test	17 8° C.	

The oil is used for soap-making and cloth-making.

STILLINGIA OIL [1] (TALLOW SEED OIL)

French—*Huile de Stillingia.* German—*Stillingiaol.*
Italian—*Olio di Stillingia.*

For tables of characteristics see p. 90.

Stillingia oil is obtained from the seeds of *Stillingia sebifera*, Willd. (*Croton sebiferum*, L.), *Sapium sebiferum*, Roxb. In the great Chinese centres where vegetable tallow and stillingia oil are manufactured, the tree is grafted and yields fruit superior to that of the wild tree. The latter occurs largely in Formosa, but its cultivation has been entirely neglected hitherto. The mesocarp surrounding the seeds yields, on being steamed, the " Vegetable " Tallow of China (cp. below). The oil is obtained by expressing the seeds after freeing them from the vegetable tallow, and is termed by the natives *tsé-réou* or *ting-yu*. The seeds are said to yield 19·2 per cent of limpid oil, of pale yellow colour. A specimen of seeds examined in the author's laboratory yielded 23·29 per cent of oil on extraction with ether. Of the seeds freed from the mesocarp 489 go to make up a weight of 50 grams. The oil has a peculiar smell and taste resembling that of linseed oil and mustard.

The fatty acids separate on standing into a liquid and a solid portion. A specimen of mixed fatty acids examined in my laboratory yielded 25·78 of ether-insoluble bromides of the melting point 171·1° C. (*Lewkowitsch* [2]).

The specimen prepared by *Tortelli and Ruggeri* contained 6·15 per cent of free fatty acids (calculated to oleic acid) and 1·45 per cent unsaponifiable matter. A specimen examined by *Nash* [3] contained 3·1 per cent free fatty acids and 0·44 per cent of unsaponifiable matter. 1000 grms. absolute alcohol dissolve at the ordinary temperature 42·8 grms. of the neutral oil, or 48·9 grms. of the oil containing 6·15 per cent of free fatty acids.

The most characteristic property of the oil is its optical rotation, viz. − 6° 45′ in a 200 mm. tube in a *Laurent* polarimeter, corresponding to − 29·9 saccharimeter degrees.

Stillingia oil has very good drying powers, absorbing 8·72 per cent and 12·45 per cent of oxygen after two and eight days respectively in *Livache's* test. It is used in China as a high-class lighting oil and also for adulterating Chinese tung oil ; hitherto it has not been exported.

[1] " Oleum stillingiæ " is vegetable tallow (of China).   [2] *Analyst*, 1904, 112.
[3] *Analyst*, 1904, 111.

Physical and Chemical Characteristics of Stillingia Oil

Specific Gravity		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Thermal Test.		Refractive Index.	
°C.	Observer	Mgrms. KOH.	Observer.	Per cent	Observer.	c.c. 1/10 norm. KOH	Observer.	Maumene °C.	Observer.	Butyro-refractometer.	Observer.
15	0·9458	203·8	Hobein	145·6	Hobein	0·93	Tortelli and Ruggeri	136·5	Tortelli and Ruggeri	"Degrees" at 35° C.	Observer
15·5	0·9395	210·4	Nash	160·6	Tortelli and Ruggeri						
15 (water 15°=1)	0·9432		Tortelli and Ruggeri	160·7	Nash					75	Tortelli and Ruggeri
27 (water 15°=1)	0·9370		"					Spec Temp React.		Refractive Index at 25° C.	
100 (water 15°=1)	0·8737		"					267	Tortelli and Ruggeri	1·4825	Nash

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Solidifying Point		Melting Point		Neutralisation Value.		Iodine Value	
Per cent	Observer.	°C.	Observer	°C.	Observer	Mgrms KOH.	Observer	Per cent	Observer.
94·4	Tortelli and Ruggeri	12·2 (Titer test)	Tortelli and Ruggeri	14·5	Tortelli and Ruggeri	214·2	Tortelli and Ruggeri Lewkowitsch	161·9	Tortelli and Ruggeri Lewkowitsch
						206·3	"	181·8	Nash
						210·5 (Saponification value)		165·0	
								Liquid Fatty Acids.	
								178·1	Tortelli and Ruggeri Lewkowitsch
								191·1	

¹ Jean's thermometer.

WHITE ACACIA OIL [1]

French—*Huile d'acacia blanc.*   German—*Weiss-Akazienol.*
Italian—*Olio di acacia bianca.*

The seeds of the white acacia, *Robinia pseudoacacia*, L., cultivated in South Russia, yield on extraction with petroleum ether 13·3 per cent of oil.

Physical and Chemical Characteristics of White Acacia Oil

Saponification Value.	Iodine Value.	Reichert Meissl Value.
192·4	161·0	1·2

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable	Neutralisation Number	Mean Molecular Weight	Iodine Value.
91·32	200·1	280·4	160·7

The specimen examined by *Jones* contained 0·20 per cent of unsaponifiable matter. The oil possesses strong drying power, as is indicated by its high iodine value. From the total mixed fatty acids, 3·7 per cent of solid fatty acids were obtained, amongst which stearic and erucic acids were identified. The liquid fatty acids consist of oleic, linolic, and linolenic acids, linolic acid predominating. The oil is easily oxidised on exposure to the air.

GARDEN ROCKET OIL [2]—DAME'S VIOLET OIL

French—*Huile de Julienne.*   German—*Rothrepsol.*
Italian—*Olio di Hesperide.*

For tables of characteristics see p. 92.

The seeds of the garden rocket, *Hesperis matronalis*, L., contain approximately 30 per cent of oil. The freshly expressed oil is of green colour, but becomes brownish on keeping. It is odourless and possesses a somewhat bitter taste.

Garden rocket oil is expressed commercially in France and Switzerland, and is used as a burning oil.

[1] Valentin Jones, *Mitt. k. k. tech Gewerbe-Museum*, 1903, 223.
[2] De Negri and Fabris *Annali del Laborat. Chim. delle Gabelle*, 1891–92, 151.

Physical and Chemical Characteristics of Garden Rocket Oil

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Maumené Test	
At 15° C.	Observer.	°C	Observer	Mgrms KOH	Observer.	Per cent.	Observer.	°C	Observer.
0·9315	Villon	−22 to −23	Schubler	191·8	De Negri and Fabris	154·9- 155·3	De Negri and Fabris	125-127·5	De Negri and Fabris
0·9335	De Negri and Fabris								

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.	Melting Point	Iodine Value.		Observer.
° C	° C	Per cent.		
16-14	20-22	157		De Negri and Fabris

HEMP SEED OIL

French—*Huile de chènevis.*   German—*Hanföl.*
Italian—*Olio di canapa.*

For tables of characteristics see p. 94.

The seeds of the hemp plant, *Cannabis sativa,* L., yield about 30 per cent of hemp seed oil. The hemp plant is cultivated in France, Belgium, Germany, Northern Italy, Turkey, Algeria, North America, India, and Japan. The quantities of hemp seed produced in France are given in the following table :—

Cultivation and Production of Hemp Seed in France

Year	Hectares under Cultivation	Kilograms
1900	26,790	8,598,800
1901	25,760	7,976,800
1902	24,317	4,918,500
1903	22,670	9,146,000
1904	20,774	9,563,700
1905	19,341	8,847,900
1906	18,947	5,442,400
1909	14,602	6,961,300
1910	13,802	6,748,750
1911	15,486	8,821,150

Hemp seed oil is also produced in Manchuria ; but owing to the fact that the seed is grown—and harvested—together with other (wild) seed, which yields about 16 per cent of a non-drying oil, the Manchurian oil is of very low quality as regards drying powers.

The following table gives some statistical data as to the German import and export of hemp seed :—

Imports into and Exports from Germany of Hemp Seed

(In metric tons)

Imports			Exports		
From	1911.	1912	Into	1911	1912
	Tons	Tons		Tons	Tons
Austria-Hungary	1544	1147	France	1276	1863
Russia	3581	3816	Holland	124	449
China	284	1871	...	...	...

Physical and Chemical Characteristics of Hemp Seed Oil

Specific Gravity		Solidifying Point	Saponification Value		Iodine Value		Maumené Test		Refractive Index. Oleo-refractometer.	
At 15° C.	Observer	°C.	Mgrms. KOH	Observer	Per cent.	Observer	°C.	Observer	"Degrees"	Observer
0·925-0·931	Allen	Thickens at	193·1	Valenta	157·5	Benedikt	98	Maumené	+30 to +34	Jean
0·9270	Chateau	−15 and	192·8	De Negri and Fabris	140·5	De Negri and Fabris	95·96	De Negri and Fabris	+34 to +37·5 at 22° C.	Pearmain
0·9280	De Negri and Fabris	solidifies at −27	190-191·1	Lewkowitsch	148	Lewkowitsch				
					159-166	Shukoff[1]				

[1] Russian oil.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point		Melting Point		Iodine Value	
°C.	Observer	°C.	Observer	Per cent.	Observer
15	Hübl	19	Hübl	141	De Negri and Fabris
16 / 14-15	De Negri and Fabris	18-19 / 17-18	De Negri and Fabris		

Titer Test.
15·6-16·6 Lewkowitsch

The colour of the freshly expressed oil is light green to greenish-yellow, becoming brownish-yellow on keeping. Hemp seed oil contains a few per cent of solid glycerides, most likely palmitin, with a small amount of stearin or arachin. The liquid fatty acids in hemp seed oil consist, according to *Bauer, Hazura, and Grüssner,* of linolic acid and smaller quantities of oleic, linolenic (and isolinolenic ?) acids.

Pure hemp seed oil is easily identified by its high iodine absorption.

Hemp seed oil is used as a paint oil, though less frequently in this country than on the Continent. The lower qualities of hemp seed oil are stated to be used in the manufacture of varnishes [1] (in Russia). Considerable quantities used to be employed (on the Continent) for making soft soaps, which were characterised by a dark green colour.

The oil does not furnish a sufficiently hard soap with caustic soda to be used in the manufacture of hard soaps.

BUCK-THORN OIL [2]

French—*Huile de nerprun.* German—*Kreuzdornöl, Purgierwegdornöl.* Italian—*Olio di spina cervina, Olio di ramno cattartico.*

Physical and Chemical Characteristics of Buck-thorn Oil

Specific Gravity.		Reichert-Meissl Value.	Iodine Value
At ° C.		c.c. $\frac{N}{10}$ norm KOH.	Per cent.
15 (water of 4° = 1)	0 9195 (?)	0 89	155

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable. Per cent.	Mean Molecular Weight.	Iodine Value. Per cent	Acetyl Value.
95 77	288·9	160·6	25·8

This oil was prepared by extracting with ether the seeds obtained from the berries of the purging buck-thorn, *Rhamnus cathartica,* L.

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[1] Lidoff, *Chem. Revue,* 1900, 120.
[2] N. Krassowski, *Journ. Russ. Phys.-Chem. Ges.,* 1905, xxxviii. 144.

The oil thus obtained had an acid value of 5·64 and contained 0·59 per cent of unsaponifiable matter, of which 0·48 per cent consisted of "phytosterol" and 0·11 per cent of a hydrocarbon, melting at 81-82° C. and belonging to the ethane series. A detailed examination of the fatty acids gave the following result: -

	Per cent
Volatile fatty acids	0·24
Stearic acid	6.00
Palmitic acid	1·12
Oleic acid	30·10
Linolic acid	35 2
Linolenic acid (and isolinolenic ? acid)	22·4

The low specific gravity of the oil hardly corresponds with this composition.

BURDOCK OIL—BUR OIL

French—*Huile de bardane.* German—*Klettensamenol* Italian *Olio di bardana.*

This oil [1] is obtained from the seeds of *Lappa minor,* D.C. (*Arctium Lappa,* L). The seeds are of the size of linseed, but have a more spherical form. One litre of seeds obtained from the Charkoff district [2] weighed 611 grams. They consisted of 46·4 per cent of husks and 53·6 per cent of "meats" The total seeds contained 14·8 per cent of oil

The pressed oil is pale yellow. It has an odour resembling that of linseed oil, and a somewhat bitter taste. The specific gravity of the oil at 17° C. is 0·9255; its saponification value, 196·6; its iodine value, 153·6; and its *Reichert-Meissl* value, 0·95. The iodine value of the insoluble fatty acids is 162. The acid value of the specimen examined by *Lidoff* [2] was 2·0

GYNOCARDIA OIL [3]

French—*Huile de gynocardia.* German · *Gynocardiaol.* Italian—*Olio di gynocardia.*

For table of characteristics see p. 97.

The oil is obtained from the seeds of *Gynocardia odorata,* R. Br. Up to the year 1900 chaulmoogra oil was generally believed to be derived from the seeds of *Gynocardia odorata.* Hence in the earlier literature gynocardia oil was described as identical with chaulmoogra oil, until *Power,* by a close investigation of the oils derived from the seeds of the

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[1] The production of this oil, as also of poppy, nettle, and mallow seeds, by "expression," was claimed by English patent 711, 1717 (T. Smith).

[2] A. P. Lidoff, *Chem. Zeit. Rep.,* 1904, 161 ; cp. also Iwanow, *Farben-Zeit.,* 1912, 2334.

[3] Power and Barrowcliff, *Journ. Chem. Soc.,* 1905, 896

chaulmoogra family, and of the oil procured from genuine seeds of *Gynocardia odorata*, firmly established the characteristics of each individual oil. In contradistinction to the oils belonging to the chaulmoogra family, Gynocardia oil is optically inactive.

Gynocardia odorata is a native of Sikkim, Assam, and Chittagong in Bengal. In Assam the oil is sometimes expressed by the natives. The shells form 37 per cent of the total weight of the seeds. The kernels furnish by expression 19·5 per cent fatty oil calculated on the entire seed. By extracting the powdered seed with ether the yield of oil rose to 27·2 per cent.

Gynocardia oil is, at the ordinary temperature, a light yellow liquid, resembling linseed oil in its odour.

The acid value of the expressed oil was 4·9, and of the extracted oil 5·0. The unsaponifiable matter was identified as "phytosterol." The mixed fatty acids contained very small proportions of volatile acids, amongst which formic and acetic acids were recognised. The insoluble acids were found to include palmitic acid, oleic acid, linolenic acid (and isolinolenic acid ?). The liquid acids yielded the oxidation products : dihydroxystearic acid, tetrahydroxystearic acid, and isolinusic acid.

Gynocardia oil is a good drying oil.

Physical and Chemical Characteristics of Gynocardia Oil

	Specific Gravity		Saponification Value, Mgms. KOH	Iodine Value, Per cent
	At ° C			
Expressed oil . .	25°	0·925	197·0	152·8
Extracted oil .	25°	0·927	199·6	152·0

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Neutralisation Value Mgms. KOH	Iodine Value Per cent
199·8	162·6

MANKETTI OIL, MUNKUETTI OIL, NSA-SANA OIL

An oil very nearly related to Manketti oil was first obtained from the kernels of " Nsa-sana " seeds from West Africa. The seeds were stated to have been derived from a species of *Aleurites*, viz. *Ricinodendron africanum* (*Imperial Institute* [1]), or *Ricinodendron Heudelotii*. They

[1] *Bull. Imp. Inst.*, 1907, 369 ; 1909, 368.

represent small round nuts, containing inside, surrounded by a very hard and thick shell, a white soft kernel. The seeds consist of 71 parts of shells and 29 parts of kernels. The total yield of oil from the seeds was 14 per cent, the yield of oil obtainable from the kernels being 47 per cent. *A. Hébert*[1] examined specimens of *Ricinodendron africanum* seeds which yielded only 8·7 per cent of oil calculated on the fruits, although they contained 35 per cent of kernels. As the specimen of oil examined by *Hébert* is stated to have had an iodine value of 87·6, doubt must be thrown (in view of determinations by other observers) on the genuineness of the specimen. Hence *Hébert's* numbers are not reproduced here. The following characteristics were given for specimens examined by the Imperial Institute in 1907 and 1909 :—

	1907.	1909
Specific gravity at 20° C.	0 9320	0 9347
Saponification value	191·6	181 7
Iodine value	147 7	148 2
Insoluble fatty acids +unsaponifiable, per cent	95·20	94 1
Titer test of fatty acids, ° C.	35·7	34·5

The oil dries on exposure to the air at the ordinary temperature in one day and leaves a wax-like residue. The expressed cake is unsuitable for cattle food, probably owing to the presence of an alkaloid.

Early in 1911 fruits of *Ricinodendron Rauthanenii*, Schinz, originating from the Manketti tree, a native of German South-West Africa, were brought to Europe, and the most extravagant statements as to the extent of the area occupied by the tree, and the value of the oil, were made (and are still being made) in the daily press. As the yield of the oil from the whole nuts (seeds) does not amount to more than 5·5 per cent, it would appear to be hopeless to consider, from a commercial point of view, the working up of the seed, especially since the price of linseed oil, which induced these (not entirely uninterested) statements, has fallen considerably.

Specimens of the seeds examined by the author gave 35 per cent of shells and 65 per cent of kernels ; the oil calculated to the whole nut did not exceed 5·5 per cent.

Fruit examined by *Grimme*[2] showed that it consists of the following components :—

	Per cent.
Exocarp and mesocarp	32 6
Endocarp	51·5
Shell surrounding the seed	5·9
Oleaginous kernel	10 00

The seeds consisted of 37·1 per cent of shell and 62·9 per cent of kernel ; the latter yielded by extraction with ether 51·5 per cent of oil, hence the yield of oil from the total seed is 32·3 per cent, and calculated to the total fruit 5·15 per cent.

[1] *Les Matières Grasses*, 1911, 2158.   [2] *Chem. Revue*, 1913, 1.

The oil has a pleasant nutty odour, and mild taste. The following characteristics were ascertained by *Grimme* and *Thoms* :—

	Grimme.	Thoms.[1]
Oil—		
Specific gravity at 15° C.	0 9286	
Solidifying point .	−8° to −10° C.	
Saponification value	194 8	195 2
Iodine value	134 8	130 4
Reichert-Meissl value	1·24	1 08
Titration number insoluble volatile acids	0 56	0 60
Refractive index at 15° C.	1 4805	
Acetyl value		18 4
Fatty Acids—		
Insoluble fatty acids +unsaponifiable .	94 8 per cent	95 8
Solidifying point .	35-36° C.	
Melting point	41° C.	
Mean molecular weight .	285 6	
Iodine value	137 6	140 7
Refractive index at 50° C.	1 4694	

WALNUT OIL—NUT OIL

French—*Huile de noix.*   German—*Nussol, Wallnussol.*
Italian—*Olio di noce.*

For tables of characteristics see pp. 101, 102.

This oil is obtained from the seeds of the common walnut tree, *Juglans regia,* L. The fruit intended for the preparation of the oil must be allowed to ripen fully and kept two to three months before being pressed, as fresh seeds yield a very turbid oil, difficult to clarify. The kernels contain from 63 to 65 per cent of oil. According to *H Kühl* [2] German walnuts yield 56·78 per cent of oil, French walnuts 60·71 per cent. The German nuts are stated to contain 19·49 per cent of protein and 3·12 per cent of nitrogen, whereas the French contain respectively only 17·63 and 2·82 per cent. The cold-drawn oil is almost colourless, or of a pale yellowish-green tint, and has a pleasant smell and an agreeable nutty taste ; the hot-pressed oil has a greenish tint and an acrid taste and smell.

The solid glycerides of walnut oil are stated to contain myristic and lauric acids ; the liquid fatty acids of the oil consist chiefly of linolic acid, and of smaller quantities of oleic, linolenic (and isolinolenic ?) acids. *Hehner and Mitchell* obtained from 1·42 to 1·9 per cent ether-insoluble brominated glycerides in the bromide test. The statement made by *Kebler* [3] that a sample of walnut oil had the *Reichert-Meissl*

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[1] *Arbb. a. d. Pharm. Inst. d. Univ. Berlin*, 1913 (9), 225.

[2] *Pharm. Zeit.*, 1909 (54), 58.

[3] *Amer. Journ. Pharm.*, 1901, 73, 173.

value 15, requires confirmation ; all the more so as the saponification value of the sample was 190·1 to 190·5. The " phytosterol " isolated from walnut oil appears to be identical with sitosterol,[1] and has the ozone value 24·81.

One part of walnut oil dissolves in 188 parts of cold, or in about 60 parts of boiling alcohol. On cooling, crystals separate from the solution.

Walnut oil has good drying powers. Its comparatively high price acts as an incentive to adulterate it with linseed oil. The latter is detected in a suspected sample by a higher *iodine value* than the normal one, and a yield of ether-insoluble brominated glycerides (or acids) exceeding 2 per cent.[2] The presence of *cotton seed* oil, *sesamé* oil, and *arachis* oil is indicated by a low iodine absorption. Confirmation is obtained in the case of the first two oils by their characteristic colour reactions, and in the case of arachis oil by the arachidic acid test. Walnut oil, in its turn, is used as an adulterant of olive oil, its higher iodine absorption being " corrected " by the addition of lard oil.

The best qualities of walnut oil are almost colourless ; such oil is therefore preferred to any other for the making of white paints for artists. These paints are less liable to crack than the paints made with linseed oil. Poppy seed oil, which is also used in the preparation of white paints for artists, is differentiated from walnut oil by not yielding ether-insoluble brominated glycerides. Walnut oil containing notable amounts of free fatty acids is unsuitable for making paints ; such oil finds an outlet in the manufacture of soft soaps.

Bellier [3] bases the detection of poppy seed oil in walnut oil on the different solubilities of their mixed fatty acids in 70 per cent alcohol at 17°-19° C. in the presence of a definite amount of potassium acetate. Poppy seed oil contains more solid fatty acids than walnut oil, and therefore gives a more abundant precipitate. The test is made as follows :—1 c.c. of the oil is warmed with 5 c.c. of a solution of alcoholic potash, containing 16 grms. in 100 c.c. of 92 per cent alcohol, until a clear solution is obtained. The test-tube is corked and warmed in a water bath for half an hour to 70° C. Then so much of a 25 per cent solution of acetic acid is run in, as is required to neutralise exactly the 5 c.c. of alcoholic potash solution (this must be ascertained in a blank test). The test-tube is then corked, placed in water of 25° C., finally in water of 17°-19° C., being shaken frequently. Pure walnut oil gives only a minute precipitate, which hardly covers the bottom of the test-tube, whereas poppy seed oil yields a copious precipitate. *Bolavoine*,[4] however, found that only from 20 per cent upwards of poppy seed oil can thus be detected in walnut oil. Moreover, rancid oils seem to give a more copious precipitate, in even a shorter time, than neutral oils.

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[1] A. Menozzi and A. Moreschi, *Rend. R. Accad. dei Lincei*, 1910 (xix.), 187.

[2] Halphen's method (*Bull. Soc. Chem.*, 1905 (35), 571), viz. to add to the sample bromine in carbon-tetrachloride solution, is a modification of the bromide test (Vol. I. Chap. VIII.). Being a qualitative test, small amounts of linseed oil would escape detection.

[3] *Ann. chim. appliq.*, 1905, 52.

[4] *Journ. Suisse de Chimie et Pharmacie*, 1906, 15.

Physical and Chemical Characteristics of Walnut Oil

Specific Gravity		Solidifying Point.	Saponification Value		Iodine Value		Maumené Test.		Refractive Index.		Viscosity in Redwood's Viscosimeter
At °C.	Observer.	°C.	Mgrms. KOH.	Observer.	Per cent	Observer.	°C.	Observer.		Observer.	Seconds at 70 F.
										Observer.	
15	0·9265	Thickens at −12 and solidifies at −27·5	196·0	Valenta	147·9-151·7	Dieterich	101	Maumené	1·4804	Blasdale	231·8
	De Negri and Fabris Blasdale [1]		188·7	Dieterich	135·7	Hazura					Crossley and Le Sueur
15·5	0·9256		193·81-197·32	De Negri and Fabris	157·9.2-148·4	Petkow [2]			Oleo-refractometer.		
15·5	0·9259		194·4	Blasdale	144·5-145·1	De Negri and Fabris	96	De Negri and Fabris	"Degrees."	Observer.	
(water 15·5=1)			192·5	Crossley and Le Sueur	132·1	Blasdale	110	Blasdale	+25 to +36	Jean	
25	0·919	Saussure			143·1	Crossley and Le Sueur					
94	0·871	"							Butyro-refractometer		
									At °C	Observer.	
									40	64·8	Crossley and Le Sueur
									40	67·65	Petkow [2]

[1] *Journ. Soc. Chem. Ind.*, 1896, 206.   Oil from *Juglans regia* grown in California.   [2] Five samples of cold-pressed oil.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable		Solidifying Point.		Melting Point.		Iodine Value.	
Per cent.	Observer.	° C.	Observer.	° C.	Observer.	Per cent.	Observer.
95·4	Crossley and Le Sueur.	16	Hubl	20	Hübl	150·05	De Negri and Fabris
				16-18	De Negri and Fabris		
						Liquid Fatty Acids	
				15	Blasdale	167	Tortelli and Ruggeri.

Bellier's method is not an exact one, and can only give rough indications when all other methods fail. *Bellier* proposed this method with a view to detecting also other vegetable oils, such as linseed oil,[1] cotton seed oil, sesamé oil, rape oil, arachis oil, olive oil; but the methods given above will be found much more reliable.

Fouchet[2] examined a specimen of oil obtained from the seeds of a cross between *Juglans nigra* and *Juglans cinerea*. They yielded 50 per cent of an oil having the following characteristics :—

Specific gravity	0 925
Saponification value	191
Iodine value	151
Refractive index at 22° C.	1 4765
Rotary power	0
Critical temperature of dissolution in alcohol	71° C.

Fouchet states that this oil contains stearic, oleic, linolic, and linolenic acids. Linolic acid is said to form about 70 per cent of the total fatty acids.

The fatty oil of *Juglans nigra*, L., is described under the name of " Pecan oil " (Paccan oil) on p. 226.

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[1] An oil sold as " huile de noiseline " is a linseed oil containing a few per cent of nut oil

[2] *Bull. Sciences Pharm.*, 1911 (xviii.), 529.

ARBUTE SEED OIL—ARBUTUS UNEDO OIL [1]

French—*Huile d'arbouse.*   German—*Sandbeerenöl.*
Italian—*Olio di corbezzola.*

The fruits of *Arbutus unedo* are used (near Perugia) for the com-
mercial production of alcohol. The fatty oil constituting 39·03 per cent
of the seeds is retained in the still residue. The insoluble fatty acids
(including the unsaponifiable matter) amount to 92·5 per cent. They
consist of palmitic, oleic, linolic, and isolinolenic acids, the two latter
predominating. The quantitative examination of the fatty acids
carried out according to *Hazura's* method is stated to have yielded 3·43
per cent oleic acid, 53·75 per cent linolic acid, and 24·33 per cent iso-
linolenic acid. It should, however, be pointed out that this composition
cannot be reconciled with the iodine value.

Physical and Chemical Characteristics of Arbutus Unedo Oil

Specific Gravity	Solidifying Point	Saponification Value	Iodine Value	Reichert-Wollny Value.	Maumené Test	Butyro refractometer	
At C	°C	Mgrms. KOH	Per cent	c.c. $\frac{n}{10}$ KOH	C	At C.	"Degrees"
15	0 9208	27	208	117 8	0 86	103 5 (In Tortelli's apparatus, olive oil being the diluent)	25	71

LINARIA OIL [2]

French—*Huile de linaire, Huile de lin sauvage.*   German—
Leinkrautöl.   Italian—*Olio di linaria.*

The seeds of *Linaria reticulata* (belonging to the *Antirrhinea*) contain
37·5 per cent of linaria oil. *Fokin* states that the oil yields no linolic
acid.

Physical and Chemical Characteristics of Linaria Seed Oil

Specific Gravity		Saponification Value	Iodine Value.
At °C		Mgrms. KOH.	Per cent.
20 (water at 18° = 1)	0 9217	188 6	140 0

[1] G. Sam, *Atti R. Accad. dei Lincei*, Rome, 1905, xiv. [2], 619-623; *Chem. Centralbl.*, 1906, i. 373.   [2] Fokin, *Chem. Revue*, 1906, 130.

, *Physical and Chemical Characteristics of the Insoluble Fatty Acids*

Insoluble Fatty Acids + Unsaponifiable.	Specific Gravity	Solidifying Point	Melting Point	Neutralisation Value.	Iodine Value.	Acetyl Value.
Per cent	At 10° C (water 19°=1)	° C	° C	Mgrms KOH	Per cent	
91·1	0·903	13·8·5	11·22	201·1	148·5	12·3

SAFFLOWER OIL—SAFFRON OIL

French—*Huile de carthame.*   German—*Saflorol.*
Italian—*Olio di cartamo.*

For tables of characteristics see pp. 107, 108.

For table of characteristics of Indian oils see p. 106.

Safflower oil is obtained from the seeds of *Carthamus tinctorius*, L., a plant until recently cultivated all over India for the preparation of the saffron dye. The chief localities where the plant is grown are Bengal, Hyderabad, Cawnpore, Bombay, and the Punjab. Two distinct varieties are grown, *Carthamus tinctorius* and *Carthamus oxyacantha*. The characteristics of the oil from *C. tinctorius* from Mombo (German East Africa) do not differ from those given below for the Indian seeds.[1]

Leather[2] ascertained in a number of samples obtained from different provinces of India the proportion of oil. His results are summarised in the following table : --

District	Number of Samples	Oil Per cent	Weight of 100 Seeds Grams
Central Provinces	6	23·54-31·82	3·405-6·774
Bombay Presidency	9	28·79-32·23	4·21 -5·516
Madras Presidency	8	23·88-33·55	2·973-4·622
United Provinces	6	27·94-29·78	3·348-4·936
Bengal	1	22·47	3·209

[1] Fendler, *Chem. Zeit.*, 1904, No. 74.
[2] *Memoirs of the Department of Agriculture in India*, March 1907.

The cultivation of the plant has also been extended to Egypt, the Caucasus, and Turkestan, and seems to be on the increase in these countries. The seeds contain as a rule from 30 to 32 per cent of oil,[1] but owing to the thick husk, only 17 to 18 per cent of the oil are obtainable by pressing. The press cake contains, therefore, a large amount of woody fibre, as is shown by the following analysis of a pressed cake, prepared by the author on a semi-large scale.

					Per cent
Albummoids	.	.	.	.	20·11
Oil	.			.	11 91
Starch, sugar, etc.			.	.	10 83
Woody fibre	.	.		.	40·75
Moisture	.	.		.	11·60
Ash	.	.	.	.	.	4·80

This analysis points to the necessity of first decorticating the seeds, so as to lay bare the kernel which forms 40 per cent of the seed. Special machinery is required for this purpose, the ordinary Anglo-American rollers having been found unsuitable on account of the extreme hardness of the husk. An experiment carried out on a semi-large scale [2] with a special machine yielded over 31 per cent of kernels (" meats ").

The oil is prepared in India on a small scale from two kinds of fruits—the cultivated white and glossy form, and the small fruit of a mottled brown, grey, or white appearance. The oil obtained from the cultivated variety by expression in the cold is pale yellow ; it has a pleasant taste simulating that of sunflower oil, so that it can be largely used for edible purposes. Considerable quantities are pressed in India together with other seeds, especially arachis nuts.

The saturated fatty acids of safflower oil consist of palmitic and stearic acids, as ascertained by fractional precipitation with magnesium acetate of those acids which yield lead salts insoluble in ether. The high iodine value of the oil points to large amounts of unsaturated acids. *Le Sueur*,[3] examining the oil by the oxidation and bromination methods, states that the liquid fatty acids consist of oleic and linolic acids ; no evidence of the presence of linolenic acids was obtained. *Walker and Warburton*, however, ascertained in the author's laboratory [4] that whilst the oil yields no ether-insoluble brominated glycerides, the fatty acids give from 0 65 to 1·65 per cent of ether-insoluble bromides. *Tylaikoff* confirms the presence of oleic and linolenic acids by their oxidation products ; as also that of linolic acid by isolating linolic tetrabromide. The unsaponifiable matter in several specimens of oil examined in my laboratory amounted to 1·5 per cent. The true acetyl value of several samples was found to be 16·1, 12·85, and 12·78 (*Lewkowitsch*). In view of the importance this oil may acquire, a number of analyses, which have been summarised partly in the table of characteristics, may be added here.

[1] *Memoirs of the Department of Agriculture in India*, March 1907.
[2] Cp. Lewkowitsch, "Problems in the Fat Industry," *Journ. Soc. Chem. Ind.*, 1903, 590.
[3] *Journ. Soc. Chem. Ind.*, 1900, 104.   [4] *Analyst*, 1902, 237.

Indian Safflower Oils (Crossley and Le Sueur [1])

Name	Description	Source	Specific Gravity	Saponification Value	Iodine Value	Reichert Meissl Value	Insoluble Fatty Acids —Unsaponifiable	Refraction at 40°C Butyro-refracto meter	Viscosity Seconds, at 70° F	Viscosity Compared with Water	Acid Value	Optical Activity in 200 mm. tube
Carthamus tinctorius	Pressed oil	C. Provinces	0·9267	192·50	140·05	...	95·30	65·2	256·1	10·08	10·41	+8'
,,		Bengal	0·9264	193·30	144·40	...	...	...	247·8	9·76	3·68	+7'
,,	...	Punjab	0·9275	186·60	138·64	0·00	...	...	274·5	10·81	8·28	...
,,	From cultivated form	,,	0·9267	189·60	144·05	...	...	...	249·1	9·81	0·76	+10'
,,	From wild form	Hyderabad	0·9253	187·40	129·80	...	...	...			2·90	+12'
,,	By cold dry expression	Bombay	0·9277	187·90	138·60	...	...	65·2	274·7	10·79	2·58	+14'
,,	From dye plant	,,	0·9262	187·20	143·40	...	...	...	250·3	9·85	2·67	+8'
,,	From oil seed plant	Cawnpore	0·9269	191·30	149·93	0·00	...	...	249·6	9·83	6·20	+4'
,,	Var.: Thornless		0·9271	189·40	141·42	0·00	...	...	258·8	10·19	5·92	+7'
,,	Var.: Thorny		0·9251	190·52	141·12		...	...	243·0	9·57	20·02	+7'
,,	...	Madras	0·9280	192·12	142·85		95·44	...	268·8	10·58	4·12	+6'
oxyacantha	...	Punjab	0·9270	189·40	135·49		...	...	294·0	11·57	3·66	+7'

[1] *Journ. Soc. Chem. Ind*, 1898, 991.

Physical and Chemical Characteristics of Safflower Oil

Specific Gravity			Solidifying Point		Saponification Value		Iodine Value		Reichert-Meissl Value		Refractive Index		Viscosity in Redwood's Viscosimeter	
At °C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{n}{10}$ norm. KOH.	Observer.	At 16°C.	Observer.	Seconds at 70°F.	Observer.
15·5 (water at 15·5° C.=1)	0·9251-0·9280	Crossley and Le Sueur	Becomes turbid	Fendler	186·6-193·3	Crossley and Le Sueur	129·8-149·9	Crossley and Le Sueur	0·0	Crossley and Le Sueur	1·477	Tylaikoff	249·1-294	Crossley and Le Sueur
,,	0·9274	Lewko-witsch	- 18°	Lewko-witsch	192·2	Lewko-witsch	146·5	Lewko-witsch					235	Lewko-witsch
,,	0·9246	,,	not com-pletely solidi-fied at -18°	,,	190·0	,,	147·3	,,			Butyro-refracto-meter at 40° C. Degrees.			
,,	0·9250	Tylaikoff		Tylaikoff	194	Tylaikoff	127·9	Fabris[2] and Settimj	0·69-0·88	Tylaikoff	65·2	Crossley and Le Sueur		
20	0·9277	Jones[1]		Jones[1]	194·1	Jones[1]	143-144·5	Jones[1]	1·45-1·63	Jones				

[1] *Chem. Zeit.*, 1900, 272.
[2] *Atti del VI. Cong. internaz. di chimica applic.* (Settimj), Roma, 1907, vol. v. 750). The seeds yielded by extraction with ether 25 per cent of oil containing 90 per cent of liquid fatty acids.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point		Neutralisation Value		Iodine Value.	
Per cent	Observer	At 15° C	Observer.	° C.	Observer.	Mgrms. KOH	Observer	Per cent	Observer.
95·4	Crossley and Le Sueur	0 9135	Fendler	16 (Titer Test)	Lewko-witsch	199	Fendler	148·2 132·5	Fendler F. and S.
				Melting Point.		Liquid Fatty Acids.			
				16-16·5	Fabris and Setting	191·4	Fendler	159·6 159·8 140 5	Lewko-witsch Fendler F. and S.

Safflower oil possesses good drying powers, and although it cannot replace linseed oil in all its applications, it should certainly form a substitute for it in many instances, and find extended use in the manufacture of soft soap. In *Livache's* test the oil absorbed 6·4 per cent of oxygen after two days (*Tylaikoff*).

Safflower oil is heated by the natives to obtain an oil suitable for the preservation of leather vessels, ropes, etc., when exposed to the action of water. A specimen of oil thus prepared had the specific gravity 0·9634, the saponification value 188·0, and the iodine value 128·9. It therefore represents a kind of " boiled oil." The special process of preparing this " boiled oil " is carried out in India as follows:— The seeds of the wild safflower, *Carthamus oxyacantha*, are expressed in the hot, and the oil is boiled in earthenware vessels for twelve hours, during which time considerable quantities of acrolein volatilise. The " boiled " oil is immediately placed in flat dishes, partly filled with cold water, so that it solidifies to a jelly-like thick mass termed " roghan " (Afridi wax). This " boiled oil " is employed by the natives in Lahore, Delhi, Bombay, and Calcutta for the manufacture of "Afridi wax linoleum." It is also used by the natives for drawing artistic designs on woven cloth, the production of which was considered for a long time a valuable secret. The pattern is made (by the natives) by means of finely pointed staves dipped in the " roghan," which is drawn out in very fine threads, and so deposited on the cloth. When completely dry, it forms an indelible pattern.

Considerable quantities of safflower oil are used as a burning oil, notably in Egypt.

KAYA OIL [1]

French—*Huile de Kaya.*   German— *Kayaol.*
Italian—*Olio di Kaya.*

This oil is obtained from the seeds of *Torreya nucifera*, S. and Z. (*Taxaceæ*), a plant growing wild in the mountainous regions in several districts of Japan.   The seeds are of long oval shape with pointed ends, 1·5 to 2·5 cm. long, and weigh on an average 1 gram.   The black coloured husks are very hard, and enclose a pale yellow kernel covered with a reddish brown skin.   The seeds consist of 32 per cent of husks and 68 per cent of kernels.   The kernels contain on an average :— Moisture, 2·67 to 5·04 per cent ; oil, 51·07 to 51·70 per cent ; ash, 2·20 to 2·29 per cent.

The oil is prepared commercially by steaming and pressing the comminuted seeds whereby about 13 per cent of oil (by volume) are obtained.   Cold-pressed oil is pale yellow, and has a faint odour and a mild taste.   Commercial oils are yellow and have a faint resinous odour.

The following characteristics were obtained in the examination of cold-pressed and commercial oils .—

	Cold-pressed Oil.	Commercial Oils.	
		I.	II.
Oil			
Specific gravity at 15° C	0·9238	0·9233	0·9244
Saponification value	188·1	188·3	188·0
Iodine value	112·2	138·0	133·4
Reichert-Meissl value	0·93		..
Refractive index at 20° C.	1·477	1·4760	1·4757
Fatty Acids—			
Insoluble acids + unsaponifiable	95·7%	...	.
Specific gravity at 98° C.	0·8509	.	.
Neutralisation value	192·81	...	..
Mean molecular weight	290·96	..	...
Iodine value	149·5	...	..

The acid values of the three specimens were 1·5, 4·2, and 12·7 respectively.

The insoluble fatty acids deposited at the ordinary temperature some crystals, which melted into the oily part at 25° C.   In the elaïdin test no solidification was observed after two hours ; at the end of twenty-four hours only a small deposit of buttery consistence was obtained.   The mixed fatty acids contain stearic acid and linolic acid (*Kametaka* [2]).   The fatty acids are stated by *Seüchi Ueno* to consist of 9 per cent of palmitic and stearic, 19 per cent of oleic, and 72 per cent

[1] Tsujimoto, *Journ. Coll. Eng. Tokyo,* 1908, 83.   [2] *Ibid.,* 1908, xxv. Art. 4.

of linolic acids.[1] When the oil is heated in a thin layer at 100° C. for three hours, it dries to an elastic film. A " boiled " oil prepared by heating with manganese borate or resinate dries completely after twenty-four hours at the ordinary temperature.

In the bromide test no ether-insoluble hexabromide was found. *Kametaka* obtained a tetrabromide, melting at 114° C., hence the presence of linolic acid is proved.

The " cold-drawn " kaya oil is consumed as an edible oil ; the commercial qualities are used for burning, in the manufacture of papers, and as an insecticide.

INUKAYA OIL (BÉBÉ OIL [2])

French—*Huile d'inukaya.* German—*Inukayaol.*
Italian—*Olio di inukaya.*

This oil is obtained from the seeds of the inukaya tree, *Cephalotaxus drupacea*, S. and Z., an evergreen plant belonging to the family of *Taxaceæ.* The seeds are of small ellipsoidical shape ; they weigh on an average 0·59 grm., and consist of 33 per cent of brown husks and 67 per cent of light brown kernels having a resinous odour. The kernels contain :—Moisture, 4·57 per cent ; oil, 67·1 per cent ; ash, 2·2 per cent. The oil (called " *bébé* " in the Shiga and Fukui districts) is prepared by steaming and pressing the powdered seeds ; it is chiefly manufactured in the northern parts of the Shiga prefecture.

The " cold-drawn " oil (prepared in the laboratory) was a light yellow oil of slightly resinous odour, which did not solidify at –15° C. The following characteristics were determined :—

Specific gravity at 15° C.	0·9250
Saponification value	188·5
Iodine value	130·3
Refractive index at 20° C.	1·476

Inukaya oil resembles kaya oil in many of its properties, but dries less readily than the latter.

On account of its resinous odour the oil cannot be used as an edible oil. It is employed in the same manner as commercial kaya oil.

ECHINOPS OIL (THISTLE [3] SEED OIL)

French—*Huile de chardon.* German—*Echinopsol.*
Italian—*Olio di echinops.*

The seeds of *Echinops ritro*, D.C. (a plant belonging to the family of *Compositæ*, and indigenous to Asia and the Mediterranean), yield 27·5 per cent of this oil.

[1] *Chem. Revue*, 1913, 208.
[2] Tsujimoto, *Journ. Coll. Eng. Tokyo*, 1908, 85.
[3] This must not be confounded with "Castilla thistle" oil from *Cynara carduuculus.* See table, "Lesser known non-drying oils."

The characteristics found by *Wijs* [1] in specimens of the oil, containing 4·4 per cent and 7·3 per cent of free fatty acids respectively, are given in the following tables.

The oil absorbs 9 per cent of oxygen (*Weger's* method). 1000 c.c. of absolute alcohol at 15° C. dissolve 51 grms. of the neutral oil (freed from fatty acids). The acetyl value of one specimen was 26·5.

The oil gives neither the *Halphen* nor the *Baudouin* reaction.

Physical and Chemical Characteristics of Echinops Oil

Specific Gravity.	Saponification Value	Iodine Value
At 20° C (Water 4°=1)	Mgrms KOH	Per cent
0·9285-0 9253	189 2 190	138 1-111 2

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Melting Point.	Neutralisation Value	Mean Molecular Weight	Iodine Value
° C.	Mgrms. KOH		Per cent
11-12	192·3-192·9	291-292	139·1-143·8

SOJA BEAN OIL, SOYA [2] BEAN OIL (SOY-BEAN OIL, BEAN
OIL, CHINESE BEAN OIL)

French –*Huile de soja, Huile de soya.* German– *Saubohnenfett, Sojabohnenol, Chinesisches Bohnenol.* Italian– *Olio di soia.*

For tables of characteristics see p. 116.

This oil is obtained from the seeds of *Dolichos soja*, L., *Soja hispida*, Sieb. et Zucc., *Soja japonica*, Savi, *Glycine hispida*, Maxim (" Sachuea bean "), *Glycine Soja*, L., a plant indigenous to China, Manchuria, Korea, Japan, Formosa, and Indo-China,[3] where the oil and the expressed cake have always been used for edible purposes.[4]

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1903, 492

[2] The Latin name "Soja" having been pronounced in this country "Soya," the spelling "Soya" has been adopted as the official one by the Chambers of Commerce in this country

[3] *Bulletin Économique de l'Indo-Chine*, December 1905 ; *Les Cultures vivrières au Tonkin*, Hanoi, 1905.

[4] O. Nagel, *Journ. Soc. Chem. Ind.*, 1903, 1337. For soya bean preparations see K. Saito, *Zentralbl. f. Bakterien und Parasitenkunde*, 1906, ii 17, 20, 101, 152.

The industry of the soya bean still forms one of the most important manufactures of Manchuria,[1] and of Japan. In China the soya bean has been cultivated for at least 4700 years, the Emperor Shen Nung having planted the soya bean about 2800 B.C. Four varieties of soya (*téou* ; *tau*) are known in China, namely, white (*pak*), yellow (*houang*), green (*tsin*), and black (*hei*). In Manchuria the beans are soaked in water over night, then crushed and boiled with a little water, so as to burst the oil cells. The oil is then expressed in the most primitive fashion ; but owing to the long time the cakes are allowed to remain in the presses the yield of oil amounts to 13 per cent, whereas modern machinery (Anglo-American presses) yield no more than 10 per cent. The expressed meal is made in the Far East into bean-cakes or bean-cheese (Chinese, *Téou-fou-tcha* ; Japanese, *Tofu*), which not only constitute one of the staple foods of the country, but form an important article of export. Thus in 1903 there were shipped from Newchwang alone 196,680 tons of beans, 6000 tons of soya bean oil, and 273,000 tons of bean-cake.[2]

The plant is also extensively cultivated in Japan[3] The extent of the soya bean industry in Japan may be gathered from the fact that there exist in that country no less than 11,000 installations, in which about two and a half million hectolitres of beans are expressed and treated per annum, by a kind of fermentation (with the aid of *Aspergillus oryzæ*), for the preparation of *Shojou* and *Misu*, liquid condiments extensively used by the population.[4] The demand for soya is so great that the Japanese home production, estimated at five to seven million hectolitres of beans per annum, does not suffice, and therefore beans are imported from Manchuria and Korea.

The following table gives the quantities of beans exported to Japan before the large shipments to Europe (see below) took place :—

Year.	Piculs [5]	Value in Dollars.
1902	1,085,000	1,629,000
1903	3,239,000	3,807,500
1904	3,654,000	4,001,500
1905	3,073,000	4,575,000
1906	4,336,000	6,458,500
1907	5,501,000	8,715,500
1908	7,761,000	10,823,000

In addition thereto considerable quantities of oil and bean-cake were sent to Japan.

[1] A. Hosie, *Manchuria*, Methuen and Co., London, 1901. Cp. also *Journ. Soc. Chem. Ind.*, 1893, 769 ; 1901, 642. N. Shaw, *The Soya Bean Industry of Manchuria*, P. S. King and Son, 1911.

[2] These statistical data are not reliable.

[3] Pozzi-Escot, *Revue gén. de chim. pur et appl.*, 1902, 64.

[4] Cp. Suzuki, Aso, and Mitarai, *Bull. Coll. Agric. Tokyo Imp. Univ.*, 1907 (7), 477. An apparatus for preparing soy sauce has been patented by Suzuki, French patent 377,294.

[5] One picul = 133·5 lbs.

Early efforts to ship soya beans to Europe were abandoned on account of the deterioration which they underwent on the long voyage, as also on account of the difficulty of disposing of the cakes.

Later efforts, after the conclusion of the Russian-Japanese War, during which enormous quantities of soya beans had accumulated in Manchuria, were more successful, and owing to favourable shipping conditions, it became practicable to send enormous quantities to England, which were readily taken up by the existing oil-crushing mills. Thus the export of soya beans from Manchuria became rapidly and firmly established, and immediately developed into a trade of enormous dimensions.

The first shipment to this country arrived in the autumn of 1908. The quantities shipped during the following years to Europe were :—

Year.					Tons.
1909	.	.	.	.	400,000
1910	.	.	.	.	500,000
1911	.	.	.	.	340,000

The quantities given for 1909 and 1910 were distributed over the several oil-milling centres as follows :—

	1909	1910
	Quarters	Quarters
London	183,636	206,100
Hull	904,998	1,082,000
Liverpool	346,847	205,150
Bristol Channel	253,035	214,850
Scotland	121,604	214,850
Sundry Ports (Rochester, etc.)	119,169	57,700
	1,929,289	1,980,650

The total shipment of beans from the Manchurian ports and from Vladivostock were as follows :—

Year					Tons.
1909	.	.	.	.	1,470,870
1910	.	.	.	.	1,200,000
1911	.	.	.	.	1,500,000

Deducting from these quantities the exports to Europe given above as, respectively, 400,000 tons, 500,000 tons, and 340,000 tons, it will be gathered that by far the largest quantities of beans are exported to Japan and China.

In the first years of the enormous shipments to Europe the total quantity of seed came almost exclusively to this country, as the heavy duties imposed by the continental countries prohibited the import. Hence the shipment of soya bean oil from this country acquired

immediately very large dimensions.   This is exemplified by the exports of oil from Hull detailed in the following table :—

To					1910.	
Austria	.	.	.	.	.	3,501 barrels
Australia	.		.	.	.	2 ,,
America	.					23,354 ,,
Belgium	.					16,068 ,,
Denmark	.					766 ,,
Egypt	.					27 ,,
France	.	,				1,500 ,,
Germany	.					16,699 ,,
Holland				.		25,537 ,,
Italy	.	.	.			11,196 ,,
India	.	.	.		.	510 ,,

The great industry which thus had sprung up almost suddenly in the working up of soya beans for oil and cake induced continental countries to abolish the duty, so that beans are now also imported to continental countries, which are thus enabled to crush these seeds side by side with cotton seed and other oleaginous seeds.

The rapid introduction of soya beans in the oil-crushing industry was especially favoured, in addition to the favourable conditions set out above, by the fact that the Anglo-American oil machinery [1] proved itself fully suitable to deal with the new product.[2]

The sudden *éclat* with which the soya bean had sprung into notoriety immediately induced endeavours to cultivate the plant as an oleaginous seed in other parts of the globe.[3]   This was facilitated by the feature that the soya plant can thrive on comparatively poor soil and does not require much attention   Thus successful efforts have been made to grow the soya plant in Ceylon, India, on the West Coast of Africa,[4] British Guiana, South Africa (Natal, Transvaal [5]), Australia, the United States,[6] Italy, and elsewhere.

The average composition of the soya bean is as follows :—

					Per cent
Oil	.	.	.		18
Water	.		.	.	30
Albuminoids	.			.	40
Carbohydrates	.	.	.	.	22
Crude fibre	.	.			5
Ash	.	.	.	.	5

The United States Department of Agriculture gives the following detailed analyses of a number of varieties of soya beans :—

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[1] Cp. L E Common and Hull Oil Manufacturing Co., English patent 5797, 1909.
[2] R Stewart and G H. Chard patented in English patent 12,727, 1910, a special mill for breaking up soya beans.
[3] *Bull. Imp. Inst.*, 1909, 309
[4] During the first season the soya bean harvested in West Africa had not deteriorated, as it yielded the full amount of oil and albuminoids.
[5] *Agric. Journ. Union S. Africa*, 1911, 279.
[6] Cp M. Toch, *Journ. Soc. Chem. Ind.*, 1912, 573.

Variety.	Oil	Water	Protein	Nitrogen free Extract	Crude Fibre	Ash.
	Per cent.	Per cent	Per cent	Per cent	Per cent	Per cent
Austin . . .	20·55	8·67	36·59	24·41	4·00	5·78
Ito San . . .	19·19	7·42	34·66	27·61	5·15	5·97
Kingston .	18·96	7·45	36·24	26·28	4·79	6·28
Mammoth . . .	21·03	7·49	32·99	29·36	4·12	5·01
Guelph . . .	22·72	7·43	33·96	25·47	4·57	5·85
Med. Yellow . .	19·78	8·00	35·54	26·30	4·53	5·85
Samarow . . .	20·23	7·43	37·82	23·65	5·05	5·82

A further most important feature which facilitated the rapidity with which the soya bean industry was introduced was that the cakes, on account of their richness in albuminoids, formed a very valuable cattle food, which in the commencement of the industry commanded a higher price even than cotton seed cakes. It was found that the cakes were especially valuable in dairies, as the milk from cows fed with soya cakes was richer in milk fat than when cotton seed cakes or even linseed cakes were used. Although in this country a certain reaction from the extravagant hopes built on this feature has set in, the export of cakes from this country for the dairy industry in Denmark, Sweden, and Norway is very considerable.

The bulk of beans are *expressed* and the cakes sold as cattle food,[1] as stated already. Not inconsiderable quantities are, however, extracted with solvents in order to obtain more oil than can be recovered by expression. This was especially remunerative when linseed and cotton seed oil stood very high in price. Extraction must further be resorted to in the case of beans which arrive in an unsound state. The extracted meal is of course only suitable as manure, although some quantities are used in the manufacture of compound cakes and have even been sold as such as cattle food on the Continent.

On an average by expression about 12 to 13 per cent of oil are re-covered. Extraction yields a larger quantity.

The expressed oil, if prepared from thoroughly sound seed, is practically neutral and can find immediate employment for soap-making, etc. If the seed has become slightly mouldy and the oil contains notable quantities of free fatty acids, a process of refining similar to that used for cotton seed oil is employed. For edible purposes the neutral oil is bleached by filtering over fuller's earth. Bleached oil for technical purposes is obtained by bleaching the crude soya bean oil with chemicals (see Chap. XIII. p. 30).

[1] The considerable quantities of soya bean available have led to an extraordinarily large number of proposals (and patents) to use the expressed cake for the most varied alimentary purposes. As this industry falls outside the scope of this work, it need only be pointed out that the most exorbitant claims were made both as to application of the cake as food-stuff and as to advantages to be obtained therefrom. It is therefore not surprising to find that ground cake is used for adulteration (e.g. of ground coffee) to a very considerable extent.

Physical and Chemical Characteristics of Soya Bean Oil

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Maumené Test		Refractive Index	
At 15°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent	Observer.	°C.	Observer.	At 40°	Observer.
0.9242	De Negri and Fabris	−15 to −8	De Negri and Fabris	192.5	De Negri and Fabris	124.4	Shukoff³	87-88	Oettinger and Buchta⁶	1.4680	Matthes and Dahle
0.924	Shukoff¹			190.6	Shukoff	137-143	Lewkowitsch⁵				
0.9250	Lewkowitsch			192	Lewkowitsch						
0.9222 to 0.9279	Toch										

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point		Melting Point		Iodine Value		Refractive Index	
Per cent.	Observer	Titer Test	Observer	°C	Observer	Per cent	Observer	At 57.5	Observer
95.5	Matthes and Dahle	21.2° C.	Lewkowitsch	27-29	De Negri and Fabris	122	De Negri and Fabris	1.465	Oettinger and Buchta
				26	Oettinger and Buchta				

¹ From seed grown in an experimental station in South Russia.
² From the variety known in commerce as Mammoth.
³ From the variety known in commerce as Peking.
⁴ Yellow beans Ingle. *Journ. Soc. Chem. Ind.*, 1911, states that some greenish soya beans yield an oil having an iodine value as high as 158.
⁵ Exceptionally some specimens of beans are stated to have yielded an oil having iodine values up to 156.
⁶ Green beans. *Zeits. f. angew. Chem.*, 1911, 828.

Soya bean oil contains, according to *Matthes and Dahle*,[1] 15 per cent of palmitic acid and 80 per cent of liquid acids. The latter are stated to consist of about 70 per cent of oleic acid, about 24 per cent of linolic acid, and about 6 per cent of linolenic acid. Various specimens examined in the author's laboratory gave from 3 to 5 per cent linolenic hexabromide by the original method described in Vol. I. p. 475. It was, however, required in order to obtain this yield to allow the bromide solution to stand over night. For the yield of hexabrominated glycerides cp. table, Vol. I. p. 477.

Eibner and Muggenthaler found by their method (Vol. I. p. 573) after 2 hours' standing 7·2, after 24 hours' standing 7·6, and after 48 hours' standing 7·8 per cent of hexabromide. A number of determinations of the linolic acid by means of linolic tetrabromide made in the author's laboratory (by *Menon* and by *Link*) led to 12-20 per cent of linolic acid.

The unsaponifiable matter of soya bean oil was shown by *Matthes and Dahle* [1] to contain about 55 per cent of a crystalline portion consisting of 2·4 per cent of stigmasterol.[2] This stigmasterol is undoubtedly identical with *Klobb and Bloch's* [3] " soyasterol " melting at 169° C., and about 97 per cent of sitosterol melting at 139° C. The liquid portion of the unsaponifiable matter (45 per cent) was found to consist of unsaturated oxygenated compounds (cp. Vol. I. p. 585).

Soya bean oil has no characteristic colour reaction. Stress may be laid on the fact that it does not give the *Halphen* colour reaction which is so characteristic of cotton seed oil. A few per cent of cotton seed oil in soya bean oil can be detected by means of *Halphen's* test, as has been frequently ascertained in the case of soya bean oils adulterated with cotton seed oil—where the market prices favoured such adulteration.[4]

The rapid introduction of soya bean oil into the commerce of the world was due to its soap-making qualities, as it just arrived on the market when a substitute for cotton seed oil was urgently required. In Japan the soya bean serves, as stated already, for the preparation of a condiment. The cake refuse is used as manure.[5] Small quantities of the oil are used for lighting purposes.

Soya bean oil, standing midway between linseed oil and cotton seed oil in its general and special soap-making properties, can be used as a substitute of either of these two oils, especially for soap-making purposes. In the manufacture of soft soap, soya bean oil serves as an almost complete substitute for linseed oil. In the manufacture of hard soaps

[1] *Archiv. d. Pharm.*, 1911, 249, 424.

[2] This disposes of erroneous statement to the contrary occurring in the literature of this subject.

[3] *Bull. Soc. Chim.*, 1907 (4), i. 422 ; cp. also Welsch, *Inaug. Dissert.*

[4] L. Setting (*Ann. Lab. Gabelle*, 1912 (6), 461) considers the following reaction as characteristic : —When 5 c.c. are treated with 2 c.c. of chloroform and 3 c.c. of a two per cent aqueous solution of uranium nitrate, the mixture yields on shaking an intensely lemon yellow-coloured emulsion.

[5] P. Takeuchi, *Journ. Coll. Agric. Imp. Univ. Tokyo*, 1909, 1, who found a " urease " in soya beans, suggests its use for the conversion of the nitrogen of urea into ammonium sulphate for manurial purposes.

it can replace cotton seed oil to some extent only, as the soap is softer than the one made from cotton seed oil.

Soya bean oil from fresh beans yields a cheap edible oil, which has to a large extent replaced cotton seed oil, and is therefore either sold as such, or in admixture with cotton seed oil as an edible oil.

When prices of linseed and cotton seed oils were abnormally high, soya bean oil was largely used for adulterating linseed oil, and even in Japan it was used for adulterating Japanese rape oil. It was then also employed extensively in the manufacture of " boiled oils " (" paint oils "), " blown oil," of varnishes, india-rubber substitutes, and also in the linoleum industry, for by prolonged blowing soya bean oil ultimately yields a gelatinous product somewhat resembling solidified linseed oil in its consistence (cp. Vol. III. Chap. XV. " Solidified Linseed Oil ").

Samples of " boiled " soya bean oil examined in the author's laboratory had specific gravities of 0·9400 to 0·9461.

Varnishes from boiled oil prepared from soya bean oil do not give a satisfactory skin. The drying takes place slowly, although the oxygen absorption of the oil is somewhat considerable. Nevertheless soya bean oil cannot replace linseed oil (as was persistently put forward for some time) as this oil requires about four days for drying, and even then the skin is still " tacky."

In the United States soya bean oil has been largely used for making boiled oil for paints. *M. Toch* [1] states that a drier of red lead or litharge is unsuitable for soya bean oil, but good results are stated to have been obtained with a tungate drier (see Vol. III. Chap. XV. " Driers ") with those kinds of soya bean oils which have proved suitable for making drying oils according to the tests given below.

Cobalt driers are, according to *Toch*, still more useful, and can even be employed in the treatment of those soya bean oils which are not found suitable in the following tests. The characteristics of a soya bean oil suitable for making paint should be (*Toch*) : (1) when heating up to 500° F. for a few minutes the oil should become pale and remain so ; (2) when the heated oil is blown with dry air from five to seven hours it should attain a gravity of 0·960 and more.

In order to import soya bean oil free of duty into Australia the oil must be denatured by adding 25 gallons of commercial neat's-foot oil and 25 gallons of " 300° test kerosene " to 50 gallons of soya bean oil, or by adding 5 gallons of terebene and 5 gallons of turpentine to 90 gallons of soya bean oil, or by adding 25 gallons of tung oil to 100 gallons of soya bean oil. Soya bean oil intended to be used in the candle-making industry is allowed to be denatured by heating to 250° F. for half an hour with 4 per cent of sulphuric acid of no less than 1·77 specific gravity at 60°.

[1] *Journ. Soc. Chem. Ind.*, 1912, 572.

POPPY SEED OIL

French—*Huile d'œillette, Huile de parot.*   German—*Mohnol.*
Italian—*Olio di papavero.*

For tables of characteristics see pp. 123, 124.

Poppy seed oil is obtained from the seeds of the two varieties of
poppy, *Papaver somniferum,* L., viz. *P. album* and *P. nigrum,* D.C.,
by pressing.   The plant is grown extensively in Asia Minor, Persia,
India, Egypt, South Russia, and the North of France ; [1] the seeds yield
from 45 to 50 per cent of oil.

Poppy seed is also produced in Manchuria, but owing to the fact
that the seed is grown—and harvested- together with some wild seeds [2]
which yield about 16 per cent of a non-drying oil, the Manchurian oil
is of very low quality, especially as regards drying powers.   Poppy seed
grown in India and Burma contains 11 8-18·6 per cent of oil.

In France a distinction is made between *huile d'œillette* and *huile
de parot.*   The former is obtained from indigenous, or at any rate
European, poppy seed, whilst *huile de parot* designates oil obtained
from oversea seed.   Since, however, by far the greatest part of ex-
pressed oils, both of European as also of oversea origin, is used as a
table oil, all edible poppy seed oils are termed *huile d'œillette.*

By far the largest quantities of poppy seed oil are crushed in
France, both in the south (Marseilles) and in the north, and in Germany.
The importance of this industry may be gathered from the following
figures :—

Year	Poppy Seed *œillette*		Poppy Seed *parot*		
	French Production	Import into France	Import into France	Import into Marseilles	Import into Germany [3]
	Kilograms	Kilograms	Kilograms	Kilograms	Kilograms
1900	6,291,300	58,300	21,912,900	2 973,500	28,749,000
1901	4,278,100	58,600	26,194,900	5,723,300	25,920,000
1902	6,226,900	12,600	28,310,000	5,917,200	31,110,000
1903	4,368,500	31,600	27,251,600	2,997,400	33,930,000
1904	6,160,300	11,200	35,249,400	6,101,600	33,610,000
1905	5,217,500	9,700	20,829,100	3,852,400	31,990,000
1906	5,676,100	14,100	26,507,500	3,181,500	28,961,100
1907		11,300	29,158,900	4,001,500	36,267,800
1908		13,400	21,334,900		23,889,800
1909		9,300	25,789,600	2,533,194	20,345,100
1910		2,900	23,347,600	11,000	22,772,300
1911		38,600	19,440,300	2,114,000	29,650,900

[1] With regard to experiments made in Germany to produce poppy seed on a com-
mercial scale cp. Thoms, *Zeits. f. angew. Chem ,* 1908 (21), 2208.
[2] A. v. Degen (*Zeits f. Unters. d. Nahrgs- u Genussm.,* 1910, xix. 1705) reports the
occurrence of henbane seed in commercial poppy seed.   J. Moller, *Zeit. allgem. osterr.
Apoth.-Ver.,* 1912 (50). 22, states that such admixture occurs in Russian seed owing to
carelessness in harvesting ; cp. also Utz, *Chem. Revue,* 1913, 5.
[3] Mostly Indian seed.

The German imports for 1911 and 1912 are given in the following table ; it should be noted that the imports under Turkey may comprise some sunflower seed :—

From	1911	1912
Turkey .	3,814	2183
India . .	13,489	7178
China . .	1,609	520

The value of poppy seed exported from India is set out in the following table :—

Export of Poppy Seeds from India

To	1902-3	1903-4	1904-5	1905-6	1906-7	1907-8	1908-9	1909-10	1910-11	1911-12
	£	£	£	£	£	£	£	£	£	£
France . . .	285,766	283,287	265,626	171,319	212,020	374,776	303,736	314,211	415,966	278,973
Belgium . .	176,532	221,471	193,178	189,675	177,298	362,162	164,069	145,902	121,769	142,155
Other Countries .	87,375	78,306	64,064	40,500	49,164	97,801	85,567	79,311	57,801	76,327
Total . .	549,673	583,064	522,868	401,494	438,482	834,739	553,372	539,424	595,536	497,455

The chief countries of origin of the poppy seed pressed in Marseilles are the Levant (Samsoun, Smyrna, Alexandrette) and India (Bombay, Calcutta). The Levant seeds are preferred to the Indian seeds, as they yield a finer oil (cp. " Sesame Oil "), and in larger proportion. The Levant seeds are white, grey, blue, or red, and yield, pressed twice, on a large scale 39 to 40 per cent of oil. The Indian seed, which is mostly white and only rarely red, yields 36 to 38 per cent of oil in practice.

The " cold-drawn " oil, the oil of the first pressing, is almost colourless or very pale golden yellow ; this is the " white poppy seed oil " of commerce. The second quality, expressed at a higher temperature, is much inferior, and constitutes the " red poppy seed oil " of commerce.[1]

Sweet (fine) table oil is prepared by cold expression in Marseilles and in the North of France (in Lille, Arras, Douay, Cambrai). The cold-pressed oil is filtered before being placed on the market. In some of these establishments paper filters are said to be used even at present.

Poppy seed oil has little or no odour and a pleasant taste, so that it is largely used as salad oil, especially as it does not easily turn rancid. The oil of unsound quality, however, possesses an acrid taste.

The cakes resulting as a by-product are rich in nitrogen and form valuable cattle food ; mouldy cakes are employed as manure for early fruit.

The acid values of commercial samples vary from 0·7 to about 30.

According to *Tolman and Munson*[2] the solid fatty acids form 6·67 per cent of the total fatty acids. The liquid fatty acids in poppy seed oil were stated by *Hazura and Grüssner* to consist of 5 per cent of linolenic acid, 65 per cent of linolic acid, and about 30 per cent of oleic acid. Since, however, the liquid fatty acids yield practically no ether-insoluble bromides, the quantity of linolenic acid must be much less than stated above. Poppy seed oils, obtained by extraction with petroleum ether, gave, according to *Utz*,[3] much higher iodine values than found hitherto, as the following table shows :—

	Iodine Value	Refractive Index At 15° C	Butyro-refracto-meter Degrees" at 40° C
Indian poppy seed oil	153·48	1·4772	78·1
Levantine ,, ,,	157·52	1·4774	78·4
German ,, ,,	156·94	1·4774	78·1

The unsaponifiable matter in poppy seed oil is small (about 0·5 per cent), and consists chiefly of sitosterol. The crude sitosterol recrystallised eight times melted at 136-137° C. The crystallised acetate melted at 125·5-126° C. (*Bomer and Winter*). No stigmasterol was found in the unsaponifiable matter by *Klamroth*.[4]

[1] Cp. also L. Vuillart, *Annal. des Falsific*, 1909, 276.
[2] *Journ. Amer. Chem. Soc.*, 1903, 690.
[3] *Chem. Zeit.*, 1903, 1177 , 1904, 257.   [4] *Inaug. Dissert* p. 36.

Physical and Chemical Characteristics of Poppy Seed Oil

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Reichert-Meissl Value		Maumené Test		Refractive Index		Viscosity	
At °C	Observer	°C	Observer	Mgrms KOH	Observer	Per cent	Observer	c.c. 1⁄10 norm. KOH	Observer	°C	Observer	At °C	Observer	Seconds at 70° F.	Observer
15	Allen	−18	Guard	193.6	De Negri and Fabris	137.6–143.3	Dieterich	0.002	Crossley and Le Sueur	80–88	Archbutt	15	1.4773	Utz	253.9	Crossley and Le Sueur
"	De Negri and Fabris					136.8–137.6	De Negri and Fabris			87–88.5	De Negri and Fabris	20	1.4751	Harvey	259.1	
0.924–0.927	Crossley and Le Sueur			190.1	Lewkowitsch	132.6–136	Lewkowitsch					60	1.4556	Thorner		
0.927	Allen			189.0–190.6	Crossley and Le Sueur	133.7–137.12	Crossley and Le Sueur						Oleo-refractometer			
0.9255–0.9258													"Degrees" Observer			
(water at 15.5 = 1)						128.8–157.5	Utz					+23.5 to −29	Jean			
0.8738												+30 to −35	Pearmain			
(water at 15.5 = 1)												at 22° C				
												Butyro-refractometer				
												At C	Observer			
												15	73.3	Utz		
												25	71.5	Mansfeld		
													72	Bickurts, Niles		
												40	63.42	Crossley and Le Sueur		

1 Very old sample.   2 East Indian oils from the Punjab Bengal and the N.W. Provinces   3 Oil obtained by extraction

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
Per cent.	Observer	At 100° C. Water at 100°=1.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
95·38	Dietzell and Kressner	0·8886	Arch-butt	16·5	Hubl	20·5	Hubl			139	De Negri and Fabris		
94·97[1]	Crossley and Le Sueur			16·5	Thorner	20-21	De Negri and Fabris; Thorner	199	Thorner			1·4506	Thörner
						20·5	Thorner						
				Titer Test.						Liquid Fatty Acids.			
				15·4– 16·2	Lewko-witsch					149·6	Tortelli and Ruggeri		

1 East Indian oils from the Punjab, Bengal, and the N.W Provinces.

Commercial poppy seed oil is, as a rule, contaminated with small quantities of sesamé oil, owing to the seed being usually pressed in the same works in which also sesamé oil is produced. Edible poppy seed oil is at present frequently adulterated with sesamé oil [1] and also with hazel-nut oil, to improve the taste of edible oil obtained from stored seed. Both adulterants are detected by the lower *iodine absorption* of the sample; the presence of sesamé oil is confirmed by a positive *Baudouin* test.[2]

The differentiation of poppy seed oil from walnut oil is of importance in the examination of white paints. The readiest means for this purpose is furnished by the bromide test; walnut oil yields from 1·4 to 1·9 per cent of ether-insoluble brominated glycerides, whereas poppy seed oil yields none. Poppy seed contains a larger proportion of solid acids [3] than walnut oil. (With regard to *Bellier's* method cp. p. 100.)

Poppy seed oil is in its turn fraudulently added to olive oil; the high iodine value (unless masked by the addition of lard oil), in conjunction with a comparatively high specific gravity, indicate the adulteration. It is also used to adulterate peach kernel oil (*Bennett* [4]).

Mixtures consisting of 80 parts of poppy seed oil and 20 parts of beeswax are sold as fixing agents for artists' paints. A similar fixing agent is made from 100 parts of egg-yolk (frequently replaced by egg albumen) and 75 parts of poppy seed oil (*K. Lupus* [5]).

The best qualities of oil are used for edible purposes, and for the preparation of the finest paints for artists. A mixture of equal volumes of "sun-bleached" poppy seed oil and bleached "boiled" poppy seed oil is extensively used for white pigments (*Lotter* [6]). A solution of fused gum mastic and Japan wax in poppy seed oil is known in commerce as "wax oil." [7] On account of the high price of poppy seed oil only the lowest qualities, which usually contain up to 15 per cent of free fatty acids, can be employed for making potash soaps. With caustic soda poppy seed oil yields a softish soap, which used to be employed early in the last century to reduce excessive hardness of olive oil soap.[8]

ASPARAGUS SEED OIL [9]

French—*Huile d'asperge*. German—*Spargelsamenol*.
Italian—*Olio di asparaghi*.

Asparagus seed (*Asparagus officinalis*, L.) contains 15·3 per cent of a fatty oil of yellowish colour.

[1] *Chem. Zeit.*, 1903, 1177; 1904, 257.
[2] Cp. also R Royer, *Annal. des Falsific.*, 1910, 380
[3] Bellier, *Ann. Chim. analyt. appl.*, 1905, 52; *Analyst*, 1905, 132; *Chem. Centralbl.*, 1905, 965 (cp. Schlegel, *Chem. Zeit.*, 1904, 573); *Journ. Soc. Chem. Ind.*, 1905, 459
[4] *Chemist and Druggist*, 1908, 89.
[5] German patents 187,211, 211,674; cp. also Bossenroth, German patent 246,120.
[6] *Journ. Soc. Chem. Ind.*, 1895, 168.
[7] This must not be confounded with "Beeswax Oil."
[8] Such addition of poppy oil soap to olive oil soap was then considered to constitute a fraud! Cp. Lewkowitsch, *Bull. de la Soc. chimique de France*, Conférence, 1909, xxxii.
[9] W. Peters, *Arch. d. Pharm.*, 1902, 53.

Specific Gravity at 15° C	Saponification Value	Iodine Value.	Butyro-refractometer "Degrees" at 25° C
0·928	194·1	137·1	75

On exposure to the atmosphere in a thin layer the oil dries to a hard varnish-like mass.

The glycerides in asparagus seed oil consist of palmitin, stearin, olein, and linolin. The presence of olein and linolin was proved by identifying among the oxidation products of the liquid fatty acids: dihydroxystearic acid and sativic acid. It is very likely that linolenic acid also occurs in the oil.

AMOORA OIL

French—*Huile d'Amoora*. German—*Amooraol*, *Immergrunbaumol* Italian—*Olio di Amoora*.

Physical and Chemical Characteristics of Amoora Oil

Specific Gravity	Saponification Value	Iodine Value	Reichert-Meissl Value	Refractive Index	Viscosity	Insoluble Acids + Unsaponifiable
At 15° C (water at 15·5: 1)	Mgrms KOH	Per cent	c.c. 4 nor. KOH	Butyro-refractometer At 40° C "Degrees"	Number of Seconds At 70° F	Per cent
0·9386	189·7	134·86	1·64	61·5	375·8	93·23

This oil is expressed in Bengal from the seeds of *Amoora Rohituka* (*Aphanamixis Rohituka*, Roxb.), Pierre (Evergreen tree). It is a clear, reddish-brown oil, and has a slight odour, resembling that of linseed oil. The specimen examined by *Crossley and Le Sueur* [1] had the acid value 17·03. The insoluble acids and unsaponifiable amounted to 93·23 per cent.

The oil is used by the natives medicinally and also as a burning oil.

MANIHOT OIL [2]—CEARA RUBBER SEED OIL

French—*Huile de manihot*. German—*Manihotol*. Italian—*Olio di manihot*.

For table of characteristics see p. 128.

This oil is obtained from the seeds of *Manihot Glaziovii*, Mull. Arg., *Euphorbiacea*, known as an india-rubber-yielding tree. According

[1] *Journ. Soc. Chem. Ind.*, 1898, 991.
[2] Fendler and Kuhn, *Berichte d. deutsch. Pharmac. Gesellschaft*, 1905 (xv. 426.

to Wildemann [1] there are several species of *Manihot Glaziovii*, of which two at least must be recognised as true species, viz. *Manihot ceara* and *Manihot Jequié*.[2] (These species of Manihot must not be confounded with *Manihot dulcis* (*M. utilissima*), the root of which yields tapioca.)

The botanical name of the " Jequié " Manihot (a tree occurring in the south-east of Bahia [3] in the neighbourhood of the town of Jequié) is *Manihot dichotoma*, Ule. The Manihot tree is indigenous to Ceara (Brazil) and is now cultivated in East [4] and West Africa. Ceara rubber trees were the first to be tried in Ceylon as an india-rubber-yielding culture, but all trees have now disappeared, having been replaced by Hevea trees (see p. 129). The seeds have a very hard shell and simulate in size ordinary hazel nuts. The seeds obtained by *Fendler and Kuhn* from Lindi, East Africa, contained 25 per cent of kernels and 74·5 per cent of husks. The total seeds yielded 9·94 per cent of oil, 8·98 per cent being furnished by the kernels and 0·96 per cent by the husks.

Seeds obtained by *Rideal and Acland*,[5] also from East Africa, weighed on an average about half a grm. each, and consisted of 45·3 per cent of kernel and 54·7 per cent of shell. The total seed yielded 15·75 per cent of oil, the kernel alone yielding 35 per cent. The seeds contain no cyanogenetic glucoside, in contradistinction to the seeds yielding Manihot oil and Para rubber tree seed oil.

The oil is yellowish-green, its odour resembles that of olive oil. Its taste is slightly bitter. The specimen examined by *Fendler and Kuhn* had the acid value 2·18, and contained 0·9 per cent unsaponifiable matter. The specimen examined by *Rideal and Acland* was fresher still, as the acid value was 0·6 only.

In the Livache test the following numbers were found by *Fendler and Kuhn* :—

Increase in Weight after						Per cent
2 days	.	.	.	.	.	0·82
3 ,,						5·79
4 ,,			.			8·33
5 ,,	.			.	.	8·36
6 ,,		.	.	.	.	8·41
7 ,,	.	.	.	.	.	8·88

These figures notwithstanding, the oil spread in a thin layer over a glass dried only after the lapse of a few weeks. At a temperature of 55° C., however, the drying was complete after ten hours. In Brazil the expressed oil is used as a substitute for linseed oil.

The fatty acids contain (*Fendler and Kuhn*) about 10·97 per cent solid acids (of m.p. 54° C.) and 89·03 per cent (evidently found by difference) liquid fatty acids.

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[1] *Le Caoutchouc et la Gutta-percha*, 1906, in. 455.

[2] Other india-rubber-yielding species of *Manihot* are— *M. heptaphylla*, Ule (Sao Francisco Manihot) ; *M. piauhyensis*, Ule (Piauhy Manihot) ; *M. cudacca*, Mull. Arg ; *Heptima Teissonieri*, A. Chev (*M. Teissonieri*, A. Chev.).

[3] With regard to attempts to cultivate the Jequié variety cp. A Zimmermann, *Der Pflanzer*, 1907, in. 167 ; 1908, iv. 193 ; 265.

[4] Cp. E. Marckwald, *Der Tropenpflanzer*, 1912, 225.

[5] *Analyst*, 1913, 259.

Physical and Chemical Characteristics of Manihot Oil

Specific Gravity at 15° C	Solidifying Point	Melting Point	Saponification Value Mgrms KOH	Iodine Value Per cent	Refractive Index. Butyro-refracto-meter		Observer.
	°C	°C			At °C	"Degrees"	
0·9258	Turbid at 4	Below −17	188·6	137·0	40	62·9	Fendler and Kuhn
0·9238			189·1	135-137	15	1·475	Rideal and Acland

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Fatty Acids + Unsaponi-fiable	Specific Gravity at 25° C	Solidifying Point C	Melting Point. C	Neutralisa-tion Number	Saponifica-tion Number	Iodine Value	Observer.
...	0·8984	20·5	23·5	197·6	200·1	143·1	Fendler and Kuhn
						Liquid Fatty Acids	
95·1 [1]						163·6 162·5	Rideal and Acland

FUNTUMIA OIL

The seeds of *Funtumia elastica* (wild rubber from the West Coast of Africa) are small and pointed at the ends. 100 seeds weigh 4·8 grms. The husks are very thin and soft, so that decortication of the seeds would be unnecessary for pressing. Seeds from the Ivory Coast gave 20 per cent of a clear dark yellow oil (*Hébert* [2]), whereas *Rideal and Acland* [3] obtained 31·33 per cent. On cooling, a brownish white " stearine " is deposited which melts at 47° C. to a clear brown liquid. The seeds contain a cyanogenetic glucoside (cp. Para rubber tree seed oil). The oil was found slightly dextro-rotatory, presumably owing to the presence of an alkaloid. The following characteristics were found :—

[1] *Analyst*, 1913, 259.   [2] *Caoutch. et Gutta-Percha*, 1912, 6232.
[3] *Analyst*, 1913, 259.

	Rideal and Acland.	Hébert.
Oil—		
Specific gravity	0·9320	0·9290 at 15° C.
Saponification value . . .	185	139
Iodine value	138	
Refractive index at 15° . . .	1·4788	
Fatty Acids—		
Insoluble fatty acids+unsaponifiable	95·1 per cent	
Liquid fatty acids	88·9 ,,	
Iodine value of liquid acids . .	175·5	

Other characteristics given by *Hébert* are omitted here, as they cannot be correct.

PARA RUBBER TREE SEED OIL—RUBBER SEED OIL

French—*Huile de siphonia elastica, Huile d'Hevea.* German—*Para-kautschukbaumsamenol, Paragummibaumol.* Italian—*Olio (d' albero) di cacciu.*

For tables of characteristics see p. 130.

This oil is obtained from the kernels of the para rubber tree, *Hevea brasiliensis,* Müller Arg., a native of the Amazon basin in Brazil. The nuts contain about 50 per cent of kernels. They also contain a power-fully acting lipolytic enzyme (*Imperial Institute*) and a cyanogenetic glucoside resembling phaseolunatin.[1] Several samples of seeds examined in the Imperial Institute yielded about 0·048 per cent of prussic acid [2] (cp. "Linseed Oil," p. 57); hence the resulting cake would furnish about 0·09 per cent of prussic acid.

The kernels yielded to petroleum ether 42·49 per cent of oil.[3] *Schroeder* [4] obtained, also with petroleum ether, 27·5 per cent only of oil. On extracting the kernels on a large scale with ether 24·32 per cent of oil were recovered. Whereas the oil extracted with petroleum ether was pale yellow, the ether-extracted oil represented a deep green semi-solid oil from which, at 15° C., solid glycerides separated. On warming to 26° C. the oil became completely fluid ; on cooling, solid glycerides again separated at 21° C. A notable difference between the oil extracted with petroleum ether and the oil extracted with common ether is shown in the iodine values (compare table). The acid value of the ether-soluble sample was 57·4, its acetyl value 27·9, and the pro-portion of unsaponifiable matter 0·705 per cent.

Amongst the fatty acids stearic and palmitic acids were identified.

The oil is of a light yellow colour ; in its odour it resembles linseed oil. On exposure to the atmosphere in a thin layer it dries to a clear

[1] Dunstan, *Proc. Chem. Soc.,* 1907, 168.
[2] Henry and Auld, *Journ. Soc. Chem. Ind.,* 1908, 428.
[3] *Bull. Imp. Inst.,* 1903, 156.   [4] *Arch. d. Pharm.,* 1905 (243), 637.

transparent film. A specimen examined in the Imperial Institute contained 5·4 per cent of free-fatty acids.

Physical and Chemical Characteristics of Para Rubber Tree Seed Oil

Specific Gravity.		Saponification Value.	Iodine Value.		Observer
° C.					
15	0·9302	206·1 [1]	128·3 [1]	127·7 [1]	Imperial Institute
20	0·9232	198·1	117·6 [2]		Schroeder
15	0·9239	185·6	133·3		Pickles and
(water at					Hayworth [3]
15°·=1)					

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable.	Melting Point Titer Test.	Mean Molecular Weight.	Iodine Value	Observer.
95·06	...	293·3	127·3	Schroeder
96·4	33	...	...	Pickles and
				Hayworth
			Liquid Fatty Acids	
			154·2	Lewkowitsch

The fatty acids of the oil consist, according to *S. Pickles and W. P. Hayworth*, of about 14 per cent saturated (solid) acids, stearic acid (melting point 69° C.), and an acid or mixture of acids melting at 56·5° C. The 86 per cent of unsaturated (liquid) acids are stated to consist of 32·6 per cent of oleic acid, 50·9 per cent of linolic acid, and 2·5 per cent of linolenic acid.

The manufacture of a drying oil from the seeds was up to recently entirely out of the question, as the seeds were all required for planting purposes in the then rapidly developing Para rubber industry in East India, Federated Malay States, Borneo, and East Africa. According to a reliable estimate,[4] made in 1907, there were in Ceylon 45,000 acres under crop; taking 175 plants to the acre, this leads to 7,875,000 plants of various ages.

Since the productive plantations in the East have become very extensive, a larger supply of seeds is available and their export for purposes of oil production may increase, especially so as the vitality

[1] Extracted with petroleum ether.
[2] Extracted with ether.
[3] *Analyst,* 1911, 491.
[4] *Ceylon Handbook and Directory and Compendium of Useful Information for 1905–1906,* compiled and edited by J. Ferguson. Colombo: A. and J. Ferguson; reviewed in *Bull. Imp. Inst.,* 1906, vol. iii. No. 4, p. 384.

of the seeds for production of seedlings is very feeble. The high prices of linseed oil ruling recently stimulated the collection of seeds, and large parcels were sent to this country. The cost of collecting has been estimated, in an Official Report of the Director of Agriculture for the Federal Malay States,[1] to amount to 1s. 1d. for 1000 seeds; the cost of collecting and shelling 1 ton of kernels (414,400 seeds) would amount to nearly £3. It is further estimated that one ton of kernels could be delivered in this country at a cost of about £6 : 10s. In view of the presence of a cyanogenetic glucoside the cakes would most likely be unsuitable for feeding cattle, and hence would have to be used as manure.

MELIA AZEDARACH OIL [2]

French—*Huile de Melia Azedarach*.   German—*Meliaol*.
Italian—*Olio di Melia*.

This oil is obtained from the seeds of *Melia Azedarach*, L. (Persian lilac; Bead tree; " Laurier grec "; " Lilas des Indes "; Sykomore [3]), which contain 39·36 per cent of oil. The total amount of oil obtainable from the fruits is 4·62 per cent. This oil must not be confounded with Margosa oil, from *Melia Azadirachta*, L. (see " Vegetable Fats ").

Specific Gravity at 15° C	Solidifying Point ° C.	Melting Point ° C.	Saponification Value.	Iodine Value	Reichert-Meissl Value	Refractive Index Butyro-refractometer " Degrees "
						At 40° C
0·92·5	- 12°	- 3	191·5	135·6	0·77	65·1

Solidifying point of the fatty acids   .   .   .   19° C.
Melting point of the fatty acids   .   .   .   22° C.

CROTON ELLIOTIANUS OIL [4]

The seeds of *Croton Elliotianus* furnished an oil having the following characteristics :—

Specific gravity at 15° C.   .   .   .   .   0·9266
•Saponification value   .   .   .   .   . 201·5
Iodine value   .   .   .   .   . 138·5
Insoluble acids + unsaponifiable   .   .   94 per cent
Titer Test   .   .   .   .   . 13·7° – 13·8° C.
The specimen had the acid value   .   .   .   4·24

The above numbers show that this oil differs considerably from the ordinary croton oil, which is derived from *Croton Tiglium*, L.

[1] *Bull. Imp. Inst.*, 1911, 36.   [2] Fendler, *Apotheker Zeit.*, 1904, 55.
[3] Watt, *Dictionary*, v. p. 223.   [4] *Bull. Imp. Inst.*, 1907, 237.

HENBANE SEED OIL [1]

French—*Huile de jusquiame*.   German—*Bilsenkrautsamenöl*.
Italian—*Olio di giusquiamo*.

Henbane seed oil is obtained from the seeds of *Hyoscyamus niger*, k.
The seeds yield about 35 per cent of oil.

The oil is yellow, slightly fluorescent, somewhat viscous, and dries
readily.

Physical and Chemical Characteristics of Henbane Seed Oil

Specific Gravity at 15° C	Saponification Value	Iodine Value.	Reichert-Meissl Value	Insoluble Acids + Unsaponifiable.
				Per cent
0·939	170·8	1·38	0·99	91·7

Recently *Utz* [2] examined a specimen of a commercial henbane seed
oil, the characteristics of which varied widely from those given above,
the iodine value being 118·7, and the saponification value 219·9, although
its *Reichert-Meissl* value was only 1·1.   A specimen of oil prepared by
Utz from the seed had an iodine value 131·3 and the remarkably high
saponification value 233·3.   The *Reichert-Meissl* value of this specimen
of oil was not determined.   Its refractive index at 15° was 1·4788.

MILLET SEED OIL

French—*Huile de millet*.   German—*Hirsenöl*.   Italian—*Olio
di miglio* ; *Olio di panico*.

Fabris and Settimj [3] obtained by extraction of the powdered grains
of millet (*Panicum italicum*) with ether, 3·5 per cent of a turbid oil.
The filtered oil is brownish-yellow ; its odour resembles that of oils
from cereals.   It is insoluble in cold absolute alcohol, but dissolves
in boiling absolute alcohol.

The following characteristics were determined :—

Oil—
Specific gravity at 15° C.	0·9275
Solidifying point	−6° to −7° C.
Saponification value	183·8
Iodine value	130·4
Butyro-refractometer " degrees " at 25° C.	70
Maumené Test	67·5° C.

[1] Mjoen, *Arch. d. Pharm.*, 1896, 234.
[2] *Chem. Revue*, 1913, 5.
[3] *Atti del VI. Congresso internaz. di chimica applicata*, Roma, 1907, v. 754 ; cp.
also G. Kassner, *Berichte*, 1887, Ref. 558.

Fatty Acids—

Insoluble acids+unsaponifiable	.	.	95·5 per cent
Solidifying point	.	.	.	19° to 20° C.
Melting point	.	.	.	.	26° to 27° C.
Iodine value	.	.	.	.	134·3
Iodine value of the liquid fatty acids	.	146·3

The mixed fatty acids consisted of 84·5 per cent of liquid and 15·5 per cent of solid fatty acids.   With regard to " Millet Oil Acid " see Vol. I. Chap. III.

NIGER SEED OIL

French—*Huile de Niger*.   German—*Nigerol.*
Italian—*Olio di Niger.*

For tables of characteristics see p. 134.

Niger seed oil is obtained from the seeds (more correctly the *achenes*) of *Guizotia abyssinica* (L.), Cass. (*Guizotia oleifera*, D.C.), a plant belonging to the *Compositæ*.   It is indigenous to Abyssinia, and largely cultivated not only in East Africa, but also in the East and West Indies. Attempts had also been made to grow it in Germany.   The fruits are small, have a tooth-like shape, and are shining black in colour.   The seeds contain from 40 to 45 per cent of oil.   According to *Konig*, the seeds have the following average composition :—

					Per cent.
Oil .	.	.	.	.	43·08
Water	.		.	.	6·72
Albuminoids	.	.	.	.	19·42
Crude fibre .	.		.	· .	14·38
Ash .	.			.	3·54
Extractive substances	.	.	.	12·86

The oil (which first came into the English market in 1851) is yellow and has a nutty taste.   Four specimens of East Indian oils examined by *Crossley and Le Sueur* [1] had acid values ranging from 5·21 to 11·69 ; three samples were optically inactive ; the fourth showed very slight dextro-rotation.

Niger seed is crushed in Hull and in Marseilles; it is frequently pressed twice.   If the seed is first pressed in the cold, it yields an edible oil. The oil of second expression is richer in free fatty acids and is therefore used in soap-making and as a substitute for linseed oil,[2] and also for adulterating rape oil.   The best qualities are employed as edible oil.[3] It is largely used in India by the poorer classes, especially in the Deccan, as a substitute for ghee (butter fat).

[1] *Journ. Soc. Chem. Ind.*, 1898, 991.
[2] According to F. Fritz, Niger oil was tried as a substitute for linseed oil in the manufacture of linoleum when the prices of linseed oil were abnormally high.   It is stated that Niger oil is easily oxidised by blowing with air.   For the manufacture of "boiled oil" as a substitute for "boiled linseed oil," it is less suitable than soya bean oil.
[3] *Journ. Soc. Chem. Ind.*, 1905, 358.

Physical and Chemical Characteristics of Niger Seed Oil

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Reichert-Meissl Value		Maumené Test		Refractive Index		Viscosity	
at ° C.	Observer	° C.	Observer	Mgrms KOH	Observer	Per cent	Observer	c.c. ⅒ norm. KOH	Observer	° C.	Observer	at 15° C.	Observer	Seconds at 70° F.	Observer
15·5 (water at 5·5=1) 0·9270 0·9248- 0·9263	Allen	-9	Allen	188·9- 192·2	Crossley and Le Sueur	132·9 133·5	Archbutt Wallenstein and Finck	0·11-0·63	Crossley and Le Sueur 1	81 82	Allen Baynes	1·4768	Utz	263·1- 292·6	Crossley and Le Sueur
99 (water at 5·5=1) 0·8738	Crossley and Le Sueur 1					126·6- 133·8	Crossley Le Sueur	0·88	Utz 2			Oleo-refractometer. +26 to +30 at 22° C.	Pearman		
												Butyro-refractometer. "Degrees" 63·0 at 40 C.	Crossley and Le Sueur		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Melting Point		Insoluble Acids + Unsaponifiable		Specific Gravity		Iodine Value of the Liquid Fatty Acids	
° C.	Observer	Per cent.	Observer	At 100° C. (water at 100=1)	Observer	Per cent	Observer
28·2	Utz	94·11	Crossley and Le Sueur	0·8886	Archbutt	147·5	Wallenstein and Finck

1 East Indian Oils (*Journ. Soc. Chem. Ind.*, 1898, 501).

2 *Chem. Revue*, 1911, 106. For the characters of a bleached Niger seed oil the original paper must be consulted.

SUNFLOWER OIL

French—*Huile de tournesol.*   German—*Sonnenblumenol.*
Italian—*Olio di girasole.*

For tables of characteristics see p. 136.

Sunflower oil, obtained from the (*achenes*) seeds of *Helianthus annuus*, L., is a pale yellow oil of mild taste and pleasant smell. The sunflower plant is a native of Mexico and is now largely cultivated for its oleaginous seeds in Russia, Hungary, India, and China.[1] The Hungarian [2] kernels are richer in oil than the Russian. The Hungarian seeds consist of 45-52 per cent of kernels, and 48-55 per cent of husks. The kernels contain 36·6 to 53 per cent of oil. On a practical scale 28-30 per cent of oil are recovered. The Russian seeds yield only 23 per cent of oil. The cake contains from 8 to 10 per cent of oil, and is said to form, owing to its easy digestibility and fattening properties, a valuable cattle food, comparable in this respect with linseed oil.

Attempts made in the United States to grow the plant for commercial purposes (to prepare edible oil) have not proved satisfactory ; the cultivation of the plant as an oil-producer has therefore been abandoned.

Experiments have also been made in India ; but it was found that sunflower is too costly to be grown there [3] as an oil-seed crop. Greater success appears to have attended the experiments made by the Cape Agricultural Department. In some cases a yield of 3250 lbs. of seed was obtained per acre ; it is therefore proposed to undertake the cultivation of sunflower for its seed on a commercial scale.[4]

The cold-drawn oil is clear and limpid. On hot pressing, the oil dissolves a considerable quantity of mucilaginous substances, similar in composition to the mucilage in linseed oil (see p. 59), which separate out on cooling. Hence, the hot-pressed oil, if required as burning oil, etc., must be refined. This is done with sulphuric acid, in the same manner as rape oil is refined.

Sunflower oil contains from 0·31 to 0·72 per cent of unsaponifiable matter. The liquid fatty acids consist chiefly of linolic acid, oleic acid being present in small quantities only.

[1] In the primitive mills of Manchuria (cp. "Soya Bean Oil") 26-27 per cent of oil are obtained by expression and 43-46 per cent of cakes, retaining 8-12 per cent of oil. This favourable technical result is due to the pounded seed being left in the wedge presses for more than twelve hours.
[2] R. Windisch, *Landw. Versuchsst.*, 1902, 305.
[3] D. Hooper, *The Agricult. Ledger*, 1907, No. 1.
[4] *Cape Agricult. Journ*, 1908 (25), 85, through *Bull. Imp. Inst*, 1908, 84.

Physical and Chemical Characteristics of Sunflower Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index.	
At °C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At 60° C.	Observer.
15	0·924-0·926 Allen	-16 to -18·5	Bornemann	193-194	Bornemann	122·5-133·3	Dieterich	72·75	De Negri and Fabris	1·4611	Thorner
,,	0·926 De Negri and Fabris	at -17 partially solid	Holde	188-189	De Negri and Fabris	197-120·2	De Negri and Fabris				
,,	0·9240 Holde[1]			193	Holde	135	Holde				
90	0·919 ,,			193-194	Thorner	129	Thorner				

Oleo-refractometer.		Butyro-refractometer.	
"Degrees."	Observer.	At 25° C.	Observer.
+35 at 22° C.	Pearmain	72·2	Beckurts and Seller

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	°C	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
95	Spuller	18	De Negri and Fabris	17·22	Peters	201·6	Thorner	124	De Negri and Fabris	1·4531	Thorner
		17	Thorner	22·24	De Negri and Fabris			124			
				23	Thorner			133-134	Thorner		
								Liquid Fatty Acids			
								154·3	Lewkowitsch		

1 *Journ. Soc. Chem. Ind.*, 1894, 892.

This oil dries more slowly than the above-described drying oils. The absorption of oxygen, according to *Hübl's* method, using copper powder as an oxygen carrier, takes place at the following rate :—

Absorption of Oxygen	After 2 days	After 7 days	After 30 days.
	Per cent.	Per cent.	Per cent.
Sunflower oil .	1·97	5·02	...
Sunflower oil fatty acids .	0·85	3·56	6·3

The sunflower is now chiefly cultivated in Southern Russia,[1] where the " cold-drawn " oil serves for culinary purposes. Such oil is used in Russia in the manufacture of margarine (*Jolles* [2]). The hot-expressed oil is employed in soap-making (soaps for textile purposes). Unless the oil contains a high proportion of free fatty acids it is unsuitable for soap-making by the cold process (*Lewkowitsch*). It is also used for the manufacture of Russian varnishes, and as a burning oil.

The extent of the sunflower seed and sunflower oil industry in Russia may be gathered from the fact that in the northern Caucasus [3] from 50,000 to 60,000 tons of sunflower cake are stated to have been produced during the year 1906. Most of the cake is sent to Denmark and Sweden, and the estimation in which the feeding properties of this cake are held may be gathered from the fact that the price the cake realised was between that of linseed cake and cotton seed cake. Smaller quantities of cakes are used in this country in the production of compound cakes. Sunflower oil is now obtainable in this country in considerable quantities, being refined on a commercial scale in·Hull. The seed stalks of the plant are burnt, and the carbonate of potash, which the ashes yield in considerable quantity, is exported. It is stated that in the year 190%, 2000 tons of crude carbonate of potash from this source were exported from the Caucasus.

According to an official report there existed in 1911 in the Kuban district 550 oil mills producing sunflower oil valued at £1,400,000. The chief places of production are Jekaterinodar, Armawir, and Maikop.

<center>YELLOW ACACIA OIL [4]</center>

<center>French—*Huile d'acacia jaune.*   German—*Gelb-Akazienol.*
Italian—*Olio di acacia gialla.*</center>

The seeds of the yellow acacia, *Caragœna arborescens*, Lam., largely cultivated in South Russia, yield 12·4 per cent of oil on extraction with petroleum ether. The unsaponifiable matter in the oil amounts to only 0·14 per cent.

[1] *Journ. Soc. Chem. Ind.*, 1892, 470.   [2] *Ibid.*, 1893, 92.
[3] Kuban district.
[4] Valentin Jones, *Mitt. k. k. technolog. Gewerbe-Museums*, 1903, 223.

Physical and Chemical Characteristics of Yellow Acacia Oil

Saponification Value	Iodine Value	Reichert-Meissl Value
190·6	128·9	2·7

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.	Neutralisation Number	Mean Molecular Weight	Iodine Value
93·94	199·0	280·9	131·7

By means of the lead-salt-ether method 8·74 per cent of " solid " fatty acids were obtained. Amongst these were identified palmitic, stearic, and erucic acids. The liquid fatty acids consisted of oleic and linolic acids. The less pronounced drying power of this oil, as compared with white acacia oil, is explained by the absence of linolenic acid.

SERVICE BERRY OIL—MOUNTAIN ASH BERRY OIL

French—*Huile de sorbier sauvage.* German—*Vogelbeerenöl.*
Italian—*Olio di sorba salvatica.*

The seeds of *Sorbus aucuparia*, L. (Service Berry ?),[1] contain 21·9 per cent of a fatty oil, which has a sweetish taste, is slightly yellowish, and dries on exposure to the air.

10 grms. of the seeds freed from oil gave 7·29 mgrms. hydrocyanic acid. The oil had the following characteristics :—

Specific gravity at 15° C.	0·9137
Refractive index at 15° C.	1·4753
Saponification value	208 0
Iodine value	128·5
Iodine value of the insoluble fatty acids	127·5
Neutralisation value of the insoluble fatty acids	230·2

CELOSIA OIL [2]

French—*Huile de Celosia.* German—*Celosiaöl.*
Italian—*Olio di celosia.*

This oil is obtained from the seeds of *Celosia cristata*, L., a plant indigenous to the East Indies and China ; it is a greenish-brown drying oil.

[1] L. van Itallie and C. H. Nieuwland, *Arch. d. Pharm.*, 1906 (244), 164.
[2] De Negri and Fabris, *Chem. Zeit. Rep.*, 1896, 161.

Physical and Chemical Characteristics of Celosia Oil

Solidifying Point.	Saponification Value.	Iodine Value.
– 10° C.	190·5	126·3

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point	Melting Point
21·-19' C.	27'-29° C.

ARGEMONE OIL [1]

French—*Huile de pavot épineux.*   German—*Argemoneöl.*
Italian—*Olio di argemona.*

Physical and Chemical Characteristics of Argemone Oil

Specific Gravity	Saponification Value	Iodine Value.	Reichert-Meissl Value	Refractive Index At 40° C	Viscosity in Redwood's Viscosimeter	Insoluble Acids + Unsaponifiable
At 15·5° (water 15·5 = 1)	Mgrms KOH	Per cent.	c.c. ½ norm KOH	Butyro-refractometer " Degrees "	Number of Seconds at 70° F	Per cent.
0·9247-0·9259	187·8-190·3	119·91-122·5	0·00	62·5	268·9-272	95·07

Argemone oil is obtained from the seeds of *Argemone mexicana,*[2] L., the Mexican or prickly poppy (Gamboge Thistle). The fresh oil is of orange or light yellow colour, and has a distinctive and acrid odour.

The Mexican poppy is a native of Jamaica, the Caribbean Islands, and Mexico. It was introduced into India about three centuries ago, presumably as ballast, and has now spread all over the country, and grows specially well in desert land and the saliferous soils of the United Provinces and the Punjab. The oil could therefore be obtained in practically unlimited quantities.

The seeds are about the size of rape seeds and contain 36 per cent of oil, 9 per cent of moisture, and 6 per cent of ash. *W. H. Bloemendal*[3] found in a number of seeds from Curaçoa and other countries·35-38·7

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[1] Crossley and Le Sueur, *Journ. Soc. Chem. Ind.*, 1898, 991.
[2] D. Hooper, *Agricult. Ledger*, 1907, No. 5 (1908), p. 35.
[3] *Pharm., Weekblad*, 1906, 14.

per cent of oil. By expression the seeds yield on a practical scale 25-30 per cent.

Volatile acids—acetic, butyric, and valeric—which have been stated to occur in Argemone oil, could not be detected in the two genuine specimens examined by *Crossley and Le Sueur*. These oils had the acid values 6·0 and 83·9 respectively. Hence the second specimen was completely soluble in 9 to 10 volumes of absolute alcohol at the ordinary temperature.

Argemone oil is used in medicine and as a burning oil in the East Indies. Its acrid taste and active therapeutic action preclude its employment as an edible oil. In the West Indies and in Mexico the oil is used as a lubricant and illuminant. In South America the expressed oil is used by painters, and especially for painting wood.

The seeds of *Argemone albiflora, A. speciosa, A. grandiflora, A. hispida*, and *A. Hunnemannii* from Curaçoa, Cape Verde, and St. Eustatius yield about 37 per cent of a fatty oil. The oil extracted from *A. speciosa* by means of carbon tetrachloride had the specific gravity 0·9435 at 15° C., the saponification value 200·2, the iodine value 113·3,[1] and gave a deep red colouration with nitric acid.

FIR SEED OIL

French—*Huile de pignon*.   German—*Fichtensamenöl*.
Italian—*Olio di pinoli*.

For tables of characteristics see pp. 141, 142.

" Fir seed oil " is the generic name for the oils obtained from the seeds of several kinds of coniferous trees.

With the exception of the oil from *Pinus Gerardiana*, a native of the East Indies, and the oil from *Pinus monophylla*, or *P. Fremontiana*, all the species of trees from which the oils described below are obtained are grown in Europe.

Fir seed oils are stated to dry readily, and to find application in the preparation of varnishes.

[1] W. H. Bloemendal, *Pharm., Weekblad*, 1906 (43), 342.

[TABLE

Physical and Chemical Characteristics of Fir Seed Oils

Oil from	Description of Oil	Yield Oil	Specific Gravity at 15° C.	Solidifying Point	Saponification Value	Iodine Value (Wijs)	Refractive Index	Observer.
				°C.				
Pinus sylvestris, L. (Scotch pine)	Viscous brownish-yellow, "Pine tree oil," "pine oil"	32.1	0.9326	−28 to −29	189.8	147.1	1.4704 at 35° C.	Grimme[1]
Pinus montana, Mill. (Mountain pine, Knee pine)	Thick yellow with green fluorescence	29.6	0.9318	−25 to −26	189.6	145.7	1.4698 at 35° C.	,,
Pinus cembra, L. (Siberian cedar, Stone pine[2])	Golden yellow, of pleasant taste	35.7	0.930	−20.3	191.8	159.2		v. Schmoelling[4]
Pinus cembra, L. (Swiss pine)	Viscous yellow		0.9316	−20 to −21	188.0	156.3	1.4710 at 40° C.	Grimme
Pinus picea, L. (Silver fir)	Brownish-yellow. "Pitch tree oil," "pitch oil"	32.8	0.9268	−25 to −26	190.5	120.9	1.4879 at 35° C.	,,
Pinus abies, L. (Norway spruce)	Golden yellow. "Red pine seed oil" (pinaster seed oil)	31.6 / 21.8	0.9312 / 0.9326	−26 / −22	192.0 / 192.6	120.5 / 120.0	1.4742 at 35° C. / 1.4685 at 40° C.	,, / ,,
Pinus pinea, L. (Stone pine) *Pinus Gerardiana*, Wall (Gerard's pine[2])	Thick brown							
Cupressus sempervirens, L., var. *horizontalis*, Mill (Cypress)	Greenish-yellow	30.7	0.9307	−17	191.3	118.3	1.4679 at 35° C.	,,
Thuja occidentalis, L. (American arbor vitæ)	Green oil	10.8	0.9320	−4	188.6	135.1	1.4857 at 35° C.	,,
Pinus monophylla; *P. Fremontiana* (Pinon; Grey pine)	Green oil	15.0	0.9298	−8	186.7	154.8	1.4705 at 35 °C.	,,
Pinus monophylla; *P. Fremontiana*	Brown / Light yellow		0.933		192.8 / 189	101.3 / 108	1.4769 (?) / 1.4543 at 40° C	Blasdale[5] / Adams and Holmes[6]

1 *Chem. Zeit.*, 1911, 925.
2 Forms large forests in Southern Siberia and occurs widely in the Alps and Carpathians.
3 Kryloff, *Journ. Soc. Chem. Ind.*, 1899, 501.
4 *Chem. Zeit.*, 1906, 815.   Maumené test 98 (by Archbutt's method).
5 *Journ. Soc. Chem. Ind.*, 1896, 205.
6 *Journ. Ind. Eng. Chem.*, 1913 (5), 485.   The mixed fatty acids are stated to consist of oleic, linolic, and small quantities of stearic, palmitic, and lauric acids.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Fatty Acids + Unsaponifiable		Solidifying Point.	Melting Point.	Neutralisation Value.	Mean Molecular Weight.	Iodine Value (Wijs).	Refractive Index.	Observer.
	Fatty Acids.	Unsaponifiable.							
	Per cent.	Per cent.	°C.	°C.					
Pinus silvestris, L.	91·48	2·06	−7 to −8	−10	191·3	293·3	153·6	1·4626 at 40° C.	Grimme
Pinus montana, Mill.	91·34	2·18	−4	0	191·2	293·4	150·5	1·4634 at 40° C.	„
Pinus cembra, L. (Siberian cedar, Stone Pine)			11·3	−9	193	290	161·3³		v. Schmoelling
Pinus cembra, L.	93·31	1·3	−11	−11 to −13	189·0	296·8	158·0	1·4607 at 40° C.	Grimme
Pinus picea, L. (expressed)	92·26	0·92	−15 to −16	−16 to −19	192·1	298·8	121·6	1·4895 at 35° C.	De Negri and Fabris
Pinus picea, L. (extracted)	89·75	3·43	−10 to −15	−17 to −19			121·5		
Pinus picea, L. (extracted)	··	··	−12 to −16	−17 to −19	190·4	301·5	121·8	1·4672 at 40° C.	Grimme
Pinus pinea, L.	91·51	1·53	−17 to −19	−12 to −16	194·3	288·7	120·8	1·4636 at 40° C.	„
Pinus Gerardiana, Wall.²	91·52	1·62	−19	−15 to −16	196·7	285·2	125·0	1·4613 at 40° C.	„
Cupressus sempervirens, L., var. *horizontalis*, Mill.	91·46	1·64	−3	0					„
Thuja occidentalis, L.	91·58	2·06	1	4–5	193·0	290·7	142·1	1·4795 at 40° C.	
Pinus monophylla; *P. Fremontiana*.	89·90	3·22	−7 to −8	12	185·7	302·1	155·7	1·4736 at 40° C.	Blasdale

¹ Kryloff. Amongst the solid acids palmitic acid was identified. The liquid fatty acids consist chiefly of linolic acid; oleic and linolenic acids are present in small quantities only. ² The seeds are known in commerce as "Nega or Neoza nuts." ³ Iodine value liquid fatty acids, 184.

DODDER OIL, CAMELINE OIL (GERMAN SESAMÉ OIL)

French—*Huile de cameline.*   German—*Leindotterol, Deutsches Sesamol, Rüllol.*   Italian—*Olio di cameline.*

For tables of characteristics see p. 144.

Cameline oil is obtained from the seeds of *Myagrum sativum*, Crantz. (or *Camelina sativa* (L.), Fr.), belonging to the *Cruciferæ*. The seeds yield 30 per cent of oil (*Grimme* [1]).

Several centuries ago the seed was grown all over Germany as a crop. At present it is harvested in some parts of South Germany, Belgium, Holland, Hungary, the Balkan States, and South Russia. Press cakes are shipped to this country (Liverpool) from Odessa, and are used in the manufacture of compound cakes. The seeds contain 31-34 per cent of an oil of a golden-yellow colour and having a pungent taste and smell. On exposure to the air the oil dries slowly. Boiled with litharge or manganese borate it yields a slowly drying varnish.

The low saponification value points to the presence of glycerides of erucic acid. The oil prepared by expression is free from sulphur, like the oils drawn in the cold from seeds of the *Cruciferæ* (cp. " Rape Oil," p. 243).

On account of its low price the oil is not likely to be adulterated. It is used in its turn for the adulteration of rape oil, in which it may be detected by a high iodine value. Cameline oil is naturally present in linseed oil expressed from East Indian seed (cp. p. 57).

The cold-drawn oil is occasionally employed for edible purposes. Its chief use, however, is for soap-making. It suitably replaces linseed oil for making soft soap during the winter. In summer, however, cameline oil cannot be used alone, its potash soap being liquid at a temperature below 20° C.

[1] *Chem. Revue*, 1912, 102.

Physical and Chemical Characteristics of Cameline Oil

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Maumene Test		Refractive Index	
At 15° C.	Observer.	°C.	Observer	Mgrms. KOH.	Observer.	Per cent	Observer.	°C	Observer.	At 20° C	Observer
0·9260	De Negri and Fabris			188	De Negri and Fabris	135·3	De Negri and Fabris	117	De Negri and Fabris	1·4761	Grimme
0·9259	Masse	−18	Chateau			142·4	Tortelli and Ruggeri			Oleo-refractometer.	
0·9224	Grimme	−15 to	Grimme	185·8	Grimme	135·1	Grimme			Degrees at 25° C	Observer.
0·9252	Schubler	−16									
0·9240	Jean							82	Jean	−32	Jean

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Fatty Acids + Unsaponifiable		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight		Iodine Value	
Per cent	Observer.	°C	Observer	°C	Observer	Mgrms. KOH	Observer	°C	Observer.	Per cent	Observer
		14·13	De Negri and Fabris	18·20	De Negri and Fabris					136·8	De Negri and Fabris
94·12	Grimme	15·16	Grimme	18·20	Grimme	189·6	Grimme	296·3	Grimme	138·5	Grimme
										Iodine Value of Liquid Fatty Acids	
										165·4	Tortelli and Ruggeri

WALLFLOWER SEED OIL [1]

French—*Huile de giroflée.*   German—*Goldlacksamenol.*   Italian—
Olio di leucaio giallo.

This oil is contained in the seeds of the common wallflower, *Cheiranthus Cheiri.*, L., and is obtained therefrom in a yield of 26·2 per cent as a green-coloured oil which on standing becomes brown. The fatty oil is accompanied by an ethereal oil (of the specific gravity 0·9034 and refractive index at 20° of 1·692).

The fatty oil freed from the ethereal oil has the following characteristics :—

Specific gravity at 15° C.	0 9240
Saponification value	180·3 (!)
Iodine value	124·58
Reichert-Meissl value	0·33
Titration number of insoluble volatile acids . .	1·4
Liquid unsaponifiable substances	1·43 per cent
Crystallisable unsaponifiable substances . .	0·47 ,,
Insoluble fatty acids (free from unsaponifiable) . .	93·76 ,,

The fatty acids of this oil were found to consist approximately of :— Cheiranthic acid, 65·0 per cent ; linolic acid, 30 per cent ; linolenic acid, 5 per cent. *Matthes and Boltze* obtained from the unsaponifiable matter of Cheiranthus oil, after purification with petroleum ether, 0·5 per cent of a phytosterol crystallising in well-defined plates melting at 136° C. and having the specific rotation $-31·78°$ and the iodine value (*Hübl*) 77·11. These observers give the formula $C_{27}H_{46}O + H_2O$ to this phytosterol.

MADIA OIL

French—*Huile de Madia.*   German—*Madiaol.*
Italian—*Olio di Madia.*

For tables of characteristics see p. 146.

Madia oil is obtained from the seeds of the Chilian *Madia sativa*, Mol., belonging to the *Compositæ*. This plant was cultivated successfully in South Germany on an experimental scale ; but the experiments have been discontinued. The seeds contain 32-33 per cent of a dark yellow oil, having a characteristic, not unpleasant odour.

Madia oil occupies an intermediate place between drying and semi-drying oils. With nitrous acid (elaidin test) it remains liquid ; for this reason, as also on account of its high iodine value, I have placed it amongst the drying oils. It absorbs, indeed, considerable quantities of oxygen, thereby becoming viscid.

The oil is chiefly used for burning ; it is also used for soap-making. The cold-pressed oil is employed for edible purposes.

[1] Matthes and Boltze, *Archiv d. Pharm.*, 1912, 211.

Physical and Chemical Characteristics of Madia Oil

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Maumene Test.	
At 15° C.	Observer	°C	Observer	Mgrms. KOH	Observer.	Per cent.	Observer	°C	Observer.
0·9286	Winkler	−10 to −17 (by hot pressure)	Winkler	192·8	De Negri and Fabris	117·5-119·5	De Negri and Fabris	95·99	De Negri and Fabris
0·9285	De Negri and Fabris	−12 to −15 (cold-drawn)	De Negri and Fabris						

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point		Melting Point		Iodine value	
°C.	Observer	°C.	Observer	Per cent.	Observer.
20·22	De Negri and Fabris	23·26	De Negri and Fabris	120·7	De Negri and Fabris

Lesser Known Drying Oils

STRAWBERRY SEED OIL

French—*Huile de fraisier.*   German—*Erdbeerenol.*
Italian—*Olio di fragola.*

Strawberry seeds (from *Fragaria vesca,* L.) contain 19 02 per cent of a drying oil (*Anarin* [1]). The iodine value of the insoluble fatty acids was 191-193. The fatty acids are stated to consist of 81 per cent linolic, and 10·5 linolenic and oleic acids.

Kochs [2] examined a specimen of oil the characteristics of which differ widely from those given above. Thus the specific gravity is 0·974, the iodine value 72·8, and the *Reichert-Meissl* value 13·42. The high acid value 56 indicates, as *Kochs* himself stated, that a partial oxidation (thickening) of the oil took place whilst the seeds were ground up to pulp.

Physical and Chemical Characteristics of Strawberry Seed Oil

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index at 25°.
0·93 ·5	193·7	180·3	2·1	1 4790

RASPBERRY SEED OIL

French—*Huile de framboisier.*   German—*Himbeerkernol.*
Italian—*Olio di lampone.*

The seeds of the raspberry contain 14·6 per cent of a strongly drying oil, which in *Livache's* test [3] absorbs 8·4 per cent of oxygen after two days. The liquid fatty acids consist chiefly of linolic and linolenic acids, linolic preponderating, and of small quantities of oleic and isolinolenic(?) acids. The acid value of the specimen of oil was 1·0. The unsaponifiable matter yielded 0·73 per cent (calculated to the oil) of phytosterol, of the melting point 134·5° C.

[1] Prot. *Russ. Phys. Chem. Soc.,* 1903, 213 ; *Chem. Centralbl.,* 1904, ii. 459.

[2] *Jahresb. d. Versuchs d. k. Gartnerlehranst. fur 1906-1907,* Dahlem.

[3] Krzizan, *Zeitschr. f. offentl. Chem.,* 1907 (13), 263 ; cp. J. Kochs, *Jahresb. d. Versuchs d. k. Gartnerlehranst ,* Dahlem.

Physical and Chemical Characteristics of Raspberry Seed Oil

Specific Gravity at 15° C.	Saponification Value.	Iodine Value	Reichert-Meissl Value.
0·9317	192·3	174·8	0·0

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity at 15° C.	Neutralisation Value.	Iodine Value.
0·9114	197·2	181·3
	Liquid Fatty Acids.	
	200·8	185·9

RED CURRANT SEED OIL

French—*Huile de groseille.*   German—*Johannisbeersamenol.*
Italian—*Olio di ribes.*

The dried seeds of the currant, *Ribes rubrum*, L., contain 16·9 per cent of an oil of yellowish-brown colour and of pleasant odour. The oil examined by *Kochs* [1] had the acid value 5·6, and gave the following characteristics :—

Oil—

Specific gravity at 15° C.	0·9120
Solidifying point	below − 17·5° C.
Saponification value	171·3 (!!)
Iodine value	152·5
Reichert-Meissl value	0·77
Butyro-refractometer " degrees " at 40° C.	62
Unsaponifiable	2·31 per cent

Fatty Acids—

Melting point (capillary tube)	− 20° C.
Neutralisation value	211
Iodine value	159·5

Kržižan [2] examined two specimens of Italian and of Bohemian origin respectively, with the following results :—

[1] *Jahresb. d. Versuchs d. k. Gartenlehranst. für 1906–1907,* Dahlem
[2] *Chem. Revue,* 1909, 1

	Italian Oil.	Bohemian Oil.
Oil—		
Specific gravity at 15° C. .	0·9265	0·9303
Saponification value .	189·9	186·9
Iodine value . . .	172·3	175·9
Mixed Insoluble Fatty Acids—		
Specific gravity at 15° C. .	0·9117	...
Neutralisation value .	196·3	...
Iodine value . . .	178·7	...
Acetyl value . . .	13·2	...
Liquid Fatty Acids—		
Neutralisation value .	199·9	200·6
Iodine value . . .	187·8	193·0

The Italian oil gave off sulphuretted hydrogen on decomposing the saponified oil with mineral acid, hence a fictitious *Reichert-Meissl* value (1·1) was obtained. The Bohemian oil was free from sulphur. The Italian oil contains stearic and palmitic acids (about 5 per cent), large quantities of linolic acid, and smaller quantities of oleic and linolenic acids.

The oil dries on exposure to the air at a temperature of 50° C. in seven hours to a dry, almost colourless skin (*Kochs*) The increase in weight on drying at the ordinary temperature was 8·78 per cent (*Kržižan*).

CRANBERRY SEED OIL

French—*Huile d'airelle.* German—*Preisselbeerenol.*
Italian --*Olio di mirtillo.*

The seeds of *Vaccinium vitis idæa*, L., contain 30·12 per cent of an oil having the following characteristics (*Diedrichs* [1]) :—

Oil—

Specific gravity at 15° C. . . .	0 9301
Saponification value . . .	190·1
Iodine value	169·2
Butyro-refractometer at 25° C. .	83·4
„ „ at 40° C. .	75·0

Fatty Acids—

Insoluble fatty acids + unsaponifiable .	95·7 per cent
Neutralisation value . . .	195·8
Iodine value	178·6
Butyro-refractometer at 40° C. .	60·4

The mixed fatty acid contains linolenic and linolic acids.

[1] *Zeits. f. Unters. d. Nahrgs· u. Genussm.*, 1912 (xxiv.), 575.

BILBERRY SEED OIL

French—*Huile de mirtille*.   German—*Heidelbeerenol*.
Italian—*Olio di bacola*.

The seeds of *Vaccinium myrtillus*, L., yield 31 per cent of oil having the following characteristics (*Diedrichs* [1]) :—

Oil—

Specific gravity at 15° C.	0·9331
Saponification value	190 4
Iodine value	167·2
Butyro-refractometer at 25° C. .	79 8
„ „ at 40° C. . .	71·2

Fatty Acids—

Insoluble fatty acids + unsaponifiable . .	95 7
Neutralisation value . . .	200·7
Iodine value	177·3
Butyro-refractometer at 40° C. . .	57·3

The mixed fatty acids contain linolenic acid.

HOP SEED OIL

French—*Huile de houblon*.   German—*Hopfensamenol*.
Italian—*Olio di luppolo*.

The seeds of the hop (*Humulus lupulus*, L.) contain 24·4 to 28·5 per cent of a light yellow coloured fatty oil, having iodine values ranging from 149·7 to 161·5 per cent.[2]

HAWTHORN SEED OIL, HIP OIL

French—*Huile d'églantier*.   German—*Hagebuttensamenöl*.
Italian—*Olio di rosa canina*.

The seeds of the berries of *Cratægus oxyacantha*; *Rosa canina*, etc. (known as hips), contain 9·63 per cent of an oil of pleasant smell, and of yellow to orange-yellow colour.   The oil examined by *Kochs* [3] had the acid value 4·2, and furnished the following characteristics :—

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1912 (xxiv.), 575.
[2] L. Briant and H. Harman, *Journal of the Institute of Brewing*, 1910, p. 5.
[3] *Jahresb. d. Versuchs d. k. Gartnerlehranst. fur 1906–1907*, Dahlem.

Oil—

Specific gravity at 50° C.	.	.	.	.	0·9161
Solidifying point	.	.	.	.	below − 17·5° C.
Saponification value	.	.	.	.	172·8
Iodine value .	.		.	.	152·8
Reichert-Meissl value .		.	.	.	0·44
Unsaponifiable matter	.	.	.	.	2 62 per cent
Butyro-refractometer " degrees " at 40° C.				.	67

Fatty Acids—

Neutralisation value .	.	.	.	.	202·9
Iodine value .	.	.	.	.	174·3

On exposure to the atmosphere at a temperature of 50° C. the oil dried after seven hours to a hard, almost colourless skin ; at the ordinary temperature it thickened after seven days, and was dry after ten days.

BLACKBERRY SEED OIL [1]

French—*Huile de ronce.*   German—*Brombeerkernol.*
Italian—*Olio di more.*

For tables of characteristics see p. 152.

This oil occurs to an extent of 12·6 per cent in the seeds of the blackberry. The oil obtained by extraction with petroleum ether is dark green to yellowish, and shows in reflected light a red fluorescence. The green colour is due to chlorophyll, which is difficult to remove, as the liquid fatty acids prepared by the lead-salt-ether method still exhibit an emerald-green colour with red fluorescence. The oil had an acid value of 2·03. The fatty acids were resolved by means of the lead-salt-ether method into 4·7 per cent of solid, and 91 per cent of liquid acids.

The solid fatty acids melt, after crystallisation from alcohol, at 61·5° C., and probably consist of palmitic acid. The liquid fatty acids were exhaustively examined by *Hazura's* method, and from the amount of the oxidation products obtained, the following approximate composition of the liquid fatty acids was derived :—

					Per cent.
Oleic acid	.	.	.	.	17
Linolic acid	.	.	.	.	80
Linolenic acid .	.	.	.	. about	1·5
Isolinolenic acid	.	.	.	. „	1·5

The unsaponifiable matter in the oil amounted to 0·83 per cent ; 0·6 per cent were obtained as crystallised (phytosterol) sitosterol, of the melting point 133° C. The oil has distinct drying powers ; in the *Livache* test it showed after three days an increase in weight of 6·87 per cent. The oil dries somewhat less rapidly than raspberry seed oil.

[1] Krźiźan, *Chem. Revue*, 1908, 7.

Physical and Chemical Characteristics of Blackberry Seed Oil

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.
0·9256	189·5	147·8	0·0

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity at 15° C.	Insoluble Fatty Acids + Unsaponifiable. Per cent	Mean Molecular Weight.	Iodine Value.	Acetyl Value
0·9070	96·3	280·9	155·1	13·9
		Liquid Fatty Acids		
		281·3	163·2	

MULBERRY SEED OIL [1]

French—*Huile de mûrier.* German—*Maulbeersamenol.*
Italian—*Olio di moro.*

Mulberry seed oil is a viscous oil of golden yellow colour, faint odour, and pleasant taste, obtained from the seeds of *Morus alba,* L. The seeds yield, on extraction with ether, 33 per cent of oil. Two specimens of oil, the one extracted with ether and the other obtained by expression —whereby only 24 per cent of oil was recovered—gave the following characteristics :—

---

[1] L. Prussia, *Chem. Zeit.,* 1910, 830.

	Extracted with Ether	Expressed.
Oil—		
Specific gravity at 15° C. .	0 9260	0 9245
„ „ at 100° C. .	0·8706	0·8692
(water at 15° C —1)		
Saponification value . . .	190·1	191·3
Iodine value	140·4	143·3
Reichert-Meissl value .	0·35	0·10
Butyro-refractometer at 15° C .	78·2	77·7
„ „ at 25° C .	72·5	71·9
„ „ at 40° C .	63·9	63·6
Maumené (Tortelli's Thermoleo-		
meter)	94·8	95·6
Fatty Acids—		
Insoluble acids + unsaponifiable	94·95 per cent	95·57 per cent
Specific gravity at 100° C .	0·8566	0 8544
(water at 15° C —1)		
Solidifying point °C. . .	20·8-21·2	19 2-19 6
Melting point °C . . .	23·6-25° C.	22-23° C.
Neutralisation value . .	. .	194
Saponification value . .	. .	199·8
Iodine value	. .	144·1
Mean molecular weight insoluble		
fatty acids	270·4	280·9
Iodine value of liquid fatty acids	146·5	159 9
Butyro-refractometer at 30° C .	63·2	58·5
„ „ at 40° C .	57 8	55·3
„ „ at 45° C .	55 5	51·0
Liquid fatty acids, per cent .	79·4	80·6
Solid fatty acids „	20·6	19·4

The oil is stated to be soluble in 95 per cent alcohol in the hot, in an equal volume of absolute alcohol at 39° C., as also in an equal volume of glacial acetic acid at 41° C.

In the *Livache* test, extracted oil absorbed 3·6 per cent of oxygen after six days, and 9·38 per cent after fourteen days.

WELD SEED OIL

French—*Huile de gaude.*   German—*Resedasamenol, Wausamenol.*
Italian—*Olio di guaderella.*

This oil is obtained from the seeds of the dyer's weld, *Reseda luteola*, D.C. Owing to the presence of chlorophyll, the oil has a dark greenish tint. Its specific gravity is 0·9358 (*Schübler*); its solidifying point −20° C. It has a bitter taste and nauseous odour. The oil dries easily on exposure to air. It is used as a burning oil and for making varnishes.

ISANO (UNGUEKO) OIL [1]

Isano (I'Sano) oil is obtained from the seeds of the I'Sano [2] or Ungueko,[3] *Onguekoa Gore,* Engl. ; *Ongokea Klainlana,* Pierre, a large tree of the family *Oleaceæ,* growing in the French Congo. The ground and dried seeds yield 60 per cent of oil of the specific gravity 0·973 at 23° C. It remains liquid at −15° C., is reddish in colour, has an insipid flavour and fishy smell ; it is viscous and possesses strong drying powers. *Maumené* test 115° C. The bromine value is stated to be double that of oleic acid, and the oil is said to contain 86 per cent of liquid fatty acids (the lead salts being entirely soluble in ether), consisting of 15 per cent oleic acid, 75 per cent linolic acid, and 10 per cent of isanic acid (Vol. I. Chap. III.). On saponification from 12 to 13 per cent of glycerol are said to be obtained.

Apparently identical with this oil is the oil obtained from the seeds of a tree known to the natives of the Belgian Congo as " Boleko " or " Sano." [4] The whole seeds contain about 23 per cent, and the kernels 78 per cent of oil.

MOHAMBA OIL [1]

The seeds yielding mohamba oil are very similar to those of the Isano tree, but after drying they yield only 12 per cent of an oil of the specific gravity of 0·915 at 23° C. The oil remains liquid at −15° C., is of yellow colour, fairly fluid, inodorous, and has an insipid taste. *Maumené* test 55° C.

On saponification about 9 per cent of glycerol and 90 per cent of brown unsaturated (liquid) fatty acids are obtained. From the lead salts of the acids (which are entirely soluble in ether) there was obtained a white fatty acid melting at 34°-35° C., soluble in alcohol and ether, and crystallising from the latter in laminæ. This acid absorbs about as much bromine as oleic acid does, and would therefore belong to the oleic series, but does not seem to be identical with any known acid. The liquid acids appear to consist of oleic acid, as they absorb an amount of bromine corresponding to oleic acid and give the elaïdin reaction.

The seeds of *Lawsonia alba,* Lamk.[5] (the henna plant of Western Asia, which is found wild or cultivated throughout India), contain 10·48 per cent of an oil which solidifies at 25·5° C. It has the iodine value 121·63. The oil is not likely to become a commercial product.

[1] Hébert, *Journ. Soc. Chem. Ind.,* 1896, 660. Cp. Heckel, *Les Graines grasses nouvelles ou peu connues des colonies françaises.* Paris, 1902.

[2] Local name in Loango.

[3] Local name.

[4] *Bull. Agric. du Congo Belge,* 1911 (2), 203.

[5] D. Hooper, *Journ. Proc. Asiatic Society of Bengal,* 1908, iv.

" Tannoom seeds " from *Chrozophora verbascifolia*, yield 35 per cent of a thick oil, which the Bedouins of Arabia use in place of ghee. The oil had the saponification value 200·2, the iodine value 137·0. The insoluble fatty acids had the " titer test " 30·5° C. The acid value of the specimen examined by *Hooper* [1] was 33.

(2) Semi-Drying Oils

The oils comprised in this class form an intermediate link between the drying and the non-drying oils; this is readily shown by their iodine values, which lie between those of the drying oils and the non-drying oils.

Chemically they differ from the drying oils by the absence (or practically complete absence) of linolenic acid, whilst they are differentiated from the non-drying oils by containing considerable amounts of linolic acid. The proportion of linolic acid decreases as the iodine values decrease. The members of this class appear to range themselves naturally into two groups :—

(a) Cotton Seed Oil Group.
(β) Rape Oil Group.

(a) The Cotton Seed Oil Group

The members of this group still possess distinct drying properties, although they are less pronounced than in the case of the true drying oils.

The drying power becomes more apparent on allowing the oils to dry at a somewhat elevated temperature. At the ordinary temperature maize oil and cotton oil form a viscous mass after exposure to the atmosphere for several weeks in thin layers. This group takes its name from its most prominent member, which may be considered as the type of a semi-drying oil which is characterised by a notable amount of linolic acid.

CELANDINE OIL, SWALLOW-WORT OIL

French—*Huile de chélidoine*. German—*Schollkrautol*.
Italian—*Olio di celidonia*.

This oil has been obtained from the seeds of *Chelidonium majus*, L., which contain 46·6 per cent of oil. The specimen examined by *Fokin* [2] had undergone hydrolysis to a considerable extent, as is evidenced by its high proportion of free fatty acids, viz. 50·4 per cent.

Fokin states that the oil contains no linolic acid.

[1] *Annual Report, Indian Museum*, 1907–1908, p. 13.   [2] *Chem. Revue*, 1906, 130.

Physical and Chemical Characteristics of Celandine Oil

Specific Gravity.		Saponification Value.
At ° C.		Mgrms. KOH.
19 (water 19° = 1)	0·917	198·2

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity		Solidifying Point	Melting Point	Neutralisation Value	Iodine Value.
At ° C.		° C.	° C.	Mgrms. KOH.	Per cent.
19 (water 19° = 1)	0·902	6·4	7·16	201·1	127·3

DAPHNE OIL [1]

French—*Huile de Daphne*.   German—*Daphneol*.
Italian—*Olio di daphne*.

The seeds of *Daphne Cnidium*, L. (*semen coccognidii*), and other Daphne species such as *D. Mezereum*, contain from 36 to 37 per cent of a greenish-yellow oil which dries on exposure to the atmosphere.

The solid fatty acids of the oil consist of palmitic and stearic acids; the statement that the liquid fatty acids contain in addition to oleic and linolic acids also linolenic and isolinolenic acids requires confirmation.

Physical and Chemical Characteristics of Daphne Oil

Specific Gravity at 15° C.	Saponification Value. Mgrms. KOH	Iodine Value. Per cent.
0·9237	196·5	126·1

[1] Peters, *Arch. d. Pharm.*, 1902, 240.

CLOVER OIL (RED CLOVER OIL ; WHITE CLOVER OIL)

French—*Huile de trèfle.*   German—*Kleesamenol.*
Italian—*Olio di trifoglio.*

This oil is obtained from the seeds of the clover, *Trifolium.* Two
species of clover seed, viz. *Trifolium pratense perenne,* L., red clover,[1]
and *Trifolium repens,* L., white clover, were examined by *Valentin
Jones.*[2] The seeds of the red clover yielded 11·1 per cent, and the seeds
of the white clover 11·8 per cent of oil on extraction with petroleum
ether.

Physical and Chemical Characteristics of Clover Oil

Clover Oil.	Saponification Value.	Iodine Value	Reichert-Meissl Value
Red . . .	189·9	124·3	3·3
White . .	189·5	119·7	2·5

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Clover Oil.	Insoluble Acids +Unsaponifiable	Neutralisation Value.	Mean Molecular Weight.	Iodine Value.
Red . .	93·62	198·1	283·2	126·2
White . .	93·24	197·6	283·8	122·2

The solid fatty acids of red clover oil consist of palmitic and stearic
acids. The liquid fatty acids contain oleic and linolic acids, the former
predominating.

White clover oil resembles very closely in its chemical composition
the red clover oil. The lower iodine value points to a smaller proportion
of liquid fatty acids in white clover oil.

The following twelve oils are described together, as they are all
derived from cucurbitaceous plants :—

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[1] Cp. F. B. Power and A. H. Salway, "The Constituents of Red Clover Flowers,"
Journ. Chem. Soc., 1910, 231.
[2] *Mitt. d. k. k. technolog. Gewerbe-Museums,* 1903, 223.

PUMPKIN SEED OIL

French—*Huile de courge, huile de potiron.* German—*Kürbissamenol, Kürbiskernöl.* Italian—*Olio di zucca.*

For tables of characteristics see p. 159.

Pumpkin seed oil is obtained from the seeds of *Cucurbita pepo,* L., by cold expression.

The entire seeds consist of 23·5 per cent husks and 76·5 per cent kernels (" meats "). The whole seeds contain from 35 to 37·5 per cent of oil ; the kernels yield from 47 to 48 per cent of oil. In South Russia the oil is prepared on a commercial scale by roasting the seeds and subsequently expressing the oil in the hot.[1]

The oil obtained by cold expression has a greenish colour with a faint red fluorescence, whilst that prepared commercially, as described above, is stated to be viscous and of a brownish-green colour by transmitted light, and of a deep red colour in reflected light. It should be noted that the seeds pass through various stages of drying or roasting, which no doubt exercise a considerable influence on the colour of the oil.

The oil expressed by *Power and Salway* had a cherry-red colour in layers of moderate thickness and then possessed a marked fluorescence ; in thin layers the oil appeared greenish-yellow.

The characteristics obtained for oils prepared by *Poda* by both methods agree closely with those yielded by commercial oils.

Power and Salway [2] found in an extended examination of a specimen of oil that it consisted of :—palmitic and stearic acid, as glycerides, 30 per cent ; oleic acid, as glyceride, 25 per cent ; and linolic acid, as glyceride, 45 per cent. No myristic acid was found ; nor could linusic acid be isolated from the products of oxidation so that linolenic acid may be said to be absent.—Amongst the unsaponifiable matter there was found a phytosterol of the formula $C_{27}H_{46}O$ melting at 162°-163° C. The pumpkin seed oil was optically inactive.

Strauss [3] attempted to bleach the oil (obtained by expressing the crushed seeds after heating them to 80°-90° C.) with concentrated sulphuric acid, chlorine, ozone, and sulphurous acid, but the results were not satisfactory. Other experiments, having for their object the refining of the oil with caustic soda, yielded a pale oil, but the losses due to saponification were very considerable.

[1] *Journ. Soc. Chem. Ind.*, 1898, 1054.
[2] *Journ. Amer. Chem. Soc.*, 1910 (22), 347.
[3] *Chem. Zeit.*, 1903, 527.

Physical and Chemical Characteristics of Pumpkin Seed Oil

At °C	Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Refractive Index	
		Observer	C	Observer	Mgms KOH	Observer	Per cent	Observer	Butyro-refractometer at 25°C Degrees	Observer
15	0.923-0.925	Poda[2]			188.4-190.2	Poda[2]	122.8-130.7	Poda[2]	70.2-72.51	Poda
15.5	0.9197	Graham[5]					120.5	Strauss	70.72.52	"
20	0.923	Schattenfroh	-16	Schattenfroh	188.7	Schattenfroh				
20 (water at 20=1)	0.922	Power and Salway			189.4	Power and Salway	119.7	Power and Salway		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids ± Unsaponifiable		Melting Point		Mean Molecular Weight	
Per cent	Observer	C	Observer		Observer
96.2	Schattenfroh	26.5-28.5[3]	Poda	284.7	Schattenfroh
		28.4-29.8[4]	"		

1 Mean values of cold-pressed and hot-pressed oil (Jour. Soc. Chem. Ind., 1898, 1054). 2 Ten commercial oil.
3 Point of incipient fusion 4 Point of complete fusion 5 Amer. Journ. Pharm., 1901, 352

The cold-drawn oil is used for edible purposes in Austria, Hungary, and Russia ; the oil from the large cucumber grown on the Slave Coast is said to surpass olive oil in flavour. The edible oil is frequently adulterated with linseed, cotton seed, sesamé, and rape oils. Linseed oil would be detected by its high iodine value and the bromide test ; cotton seed oil by the *Halphen* colour reaction ; sesamé oil by the *Baudouin* colour reaction ; rape oil by a low iodine value, in conjunction with a lower saponification value.

The lower qualities of pumpkin seed oil serve as a burning oil.

The seeds from the Indian pumpkin yielded 25 per cent of an oil, having the following characteristics (*Hooper* [1]) :—

Oil—

Specific gravity at 15° C.	.	.	.	0·926 ; 0·928
Saponification value .	.	.	.	195 7 ; 196·2
Iodine value .	.	.	.	126 0 ; 129 6
Reichert-Meissl value .	.	.	.	0 43 ; 0·52

Fatty Acids—

Insoluble acids + unsaponifiable	.	.	94·97 ; 94·7 per cent
Titer test	.	.	31 0° C. ; 32° C.
Acid value of the specimen examined	.	.	12·78 ; 10 86

For the oil from *Cucurbita maxima*, the " squashed gourd " of India had the following characteristics (*Hooper* [1]) :—

Oil—

Specific gravity at 15° C.	.	.	.	0·919 ; 0 926
Saponification value .	.	.	.	194·9 ; 197·1
Iodine value .	.	.	.	88·7 (?) ; 133 4
Reichert-Meissl value .	.	.	.	0·47 ; 0 67

Fatty Acids—

Insoluble acids + unsaponifiable	.	.	94 3 ; 95 8
Titer test	.	.	32° C. ; 38° C.

COLOCYNTH OIL

French—*Huile de coloquinte.*   German—*Koloquintensamenol.*
Italian—*Olio di coloquintida.*

From the colocynth seeds (*Citrullus colocynthis*, Arn.) of Baluchistan 17·8 per cent of oil are obtainable (*Hooper* [1]). The oil extracted (by means of carbon tetrachloride) from Algerian [2] seeds had to a slight degree the characteristic taste of the oils belonging to the *Cucurbitaceæ*. *Power and Moore* [3] obtained from the seeds of *Citrullus colocynthis*, Schroeder, 12·7 per cent (by extraction with petroleum ether) of a clear

[1] *Annual Report, Indian Museum*, 1907–1908, p. 13.
[2] Grimaldi and Prussia, *Bull. Chim. Farm.*, 1909 (48), p. 93.
[3] *Journ. Chem. Soc.*, 1910, 99.

pale yellow, optically inactive oil. The following characteristics were ascertained :—

	Hooper	Guinadh and Prussia	Power and Moore
Oil—			
Specific gravity at 15° C		0 9289	
,, ,, at 20° C			0 9273
(water at 20° C. l)			
Specific gravity at 100° C		0 8733	
(water at 15° C l)			
Solidifying point		– 14° C.	
Saponification value	202 9	191 7	186 7
Iodine value	129 3	120 4	126 6
Reichert-Meissl value	..	0 32	
Butyro-refractometer—			
"degrees" at 15° C		78 2	
,, at 25° C		72 3	
,, at 40° C		63 5	
Maumené test (in Tortelli's apparatus)		86 4	
Fatty Acids—			
Insoluble acids + unsaponifiable	92 2 per cent	90 72 per cent	
Specific gravity at 50° C			0 8910
(water at 50° C =1)			
Specific gravity at 100° C		0 8537	
(water at 15° C =1)			
Solidifying point	29° (titer)	26 2-27 2	
Melting point		29 2-30	29 5-32
Neutralisation value		192 6	195 6
Saponification value		198 2	..
Iodine value		121	131·1
Iodine value of liquid fatty acids	..	150	
Liquid fatty acids		56 2 per cent	
Solid fatty acids		43 8 ,,	
Butyro-refractometer—			
"degrees" at 30° C		56 7	
,, at 40° C		51 5	..
,, at 45° C		48 3	..

Power and Moore isolated from the oil a phytosterol $C_{20}H_{34}O$ melting at 159°-160° (acetate melting at 167°-170°) having $[a]_D = + 8·1°$.

The Algerian oil absorbed in *Livache's* test, after 3 days 5·22 per cent, and after 7 days 5·76 per cent, of oxygen. The acid value of the Baluchistan oil was 5 9 and that of the Algerian oil 2·7.

IKPAN SEED OIL [1]

French—*Huile d'ikpan.*   German—*Ikpansamenol.*
Italian—*Olio di semi di ikpan.*

This oil is obtained from the " ikpan seeds " of Southern Nigeria, which are probably derived from one of the forms of water melon,

[1] *Bull. Imp. Inst.*, 1907, 132, 133 ; 1908, 356.

Citrullus vulgaris, common in West Africa. The seeds consist of 36 parts of shells and 64 parts of kernels. The kernels yield 40 per cent of a pale yellow oil from which on standing some " stearine " separates. The following characteristics have been ascertained —

	I	II.
Specific gravity at 15° C.	0·9184	0·922
Saponification value	194·0	196·5
Iodine value	106·0	107·0
Insoluble fatty acids + unsaponifiable	95·9 per cent	
Titer test of fatty acids	36° C.	

Three other oils obtained from species of *Citrullus*, viz. *Citrullus naudinianus* (Hook), *Citrullus vulgaris*, and an unidentified species from West Africa, were examined by *Grimme*[1] and by *Heering and Grimme*. The characteristics of the three oils are collated in the following table :—

	Oil from		
	C. naudinianus[2]	C. vulgaris[1]	C. species (?)[1]
Oil—			
Yield of oil from seeds, per cent	15·33	15·33	11·8
Specific gravity at 15·15° C	..	0·9143	0·9158
Solidifying point, ° C.	- 7	- 5	- 11·5
Melting point, ° C.	..	- 2°	- 5
Saponification value	203·1	198·2	195·6
Iodine value (Wijs)	120·3	123·7	119·5
Refractive index at 20° C.	1·4747	1·4728	..
„ „ at 15° C	..	..	1·4751
Unsaponifiable matter, per cent	4·37	1·34	0·28
Fatty Acids—			
Insoluble acids + unsaponifiable per cent	..	94·6	95·9
Solidifying point, ° C.	..	32	33
Melting point, ° C.	32-34	34-35	34
Neutralisation value	182·2	196·2	194·5
Mean molecular weight	308·3	286·2	285·8
Iodine value	104·0	112·3	122·3
Refractive index at 40° C.	1·4647	1·4632	..
„ „ at 45° C.	..	..	1·4568

NARRAS SEED OIL

This oil is obtained from the seeds of *Acanthosicyos horrida*, Welw.[4] This species differs from all other plants belonging to the Cucurbitaceæ

[1] *Chem. Revue*, 1910, 182, 268.   [2] *Ibid.*, 1910, 182.
[1] *Chem. Zentralblatt*, 1911 (n.), 1742.
[4] Cp. Dinter, *Tropenpflanzer*, 1901, S. 474.   R. Marloch, *Englers bot. Jahrbucher*, 1888, S. 173.

by its want of leaves. The plant covers the heights surrounding Walfish Bay in hedges and shrubs rising to a height of from 3 to 5 feet. The kernels contain 47·8 per cent of a fatty oil, which had the following characteristics : [1] –

Oil—

Solidifying point, ° C.	− 7
Melting point, ° C.	−9 to − 11·5
Saponification value	181·4
Iodine value	116·6
Refractive index at 20° C.	1·4768

Fatty Acids—

Solidifying point, ° C.	26 – 16° C.
Melting point, ° C.	31-32
Neutralisation value	179·8
Iodine value	122·0
Refractive index at 40° C.	1·4581

BRYONY OIL [2]

French—*Huile de vigne blanche.*   German—*Zaunrübenöl.*
Italian—*Olio di brionia.*

The (poisonous) seeds of *Bryonia dioica,* belonging to the *Cucurbitaceæ,* contain 23·6 per cent of a viscous, reddish-yellow oil, having the following characteristics : –

Saponification value	193·0
Reichert-Meissl value	0·66
Iodine value	135·1
Butyro-refractometer, " degrees " at 25° C.	75·5
„ „ „ 40° C.	67·2

No hexabromide was obtained in the " Bromide test " (Vol. I. p. 475).

WATER-MELON OIL

French—*Huile de pasèque (huile de citrouille* [3]*), huile de gros béraff (béreff).*
German –*Wassermelonenöl.*   Italian –*Olio di citriuolo.*

The seeds of *Cucumis citrullus,* L. (*Cucurbita citrullus,* L.), yield 62 per cent of kernels containing 65·8 per cent of oil ; hence the seeds contain 40·8 per cent of oil.

Power and Salway, [4] however, found only 19 per cent of oil in the

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[1] C. Grimme, *Chem Revue,* 1910, 182.
[2] A Diedrichs, *Chem Revue,* 1912, 239.
[3] It should be noted that the name " huile de citrouille" would also apply to " pumpkin seed oil."
[4] *Journ. Amer. Chem. Soc.,* 1910 (22), 360.

entire seed ; they obtained by expression 7·4 per cent of a light yellow-coloured oil, entirely devoid of fluorescence. This oil was optically inactive. The chemical composition of this oil was as follows :— Palmitic and stearic acids, as glycerides, 30 per cent ; oleic acid, as glyceride, 25 per cent ; and linolic acid, as glyceride, 45 per cent. Of the solid acids, stearic seems to preponderate. This oil also contained a small amount of phytosterol melting at 163°-161° C. Whereas the composition of the oil closely resembles that of pumpkin seed oil, the phytosterol, although agreeing in its melting point with the phytosterol from the latter oil, has the composition $C_{20}H_{34}O$.

A specimen of oil examined by *Wijs* [1] contained 1·20 per cent free fatty acids; it gave the characteristics recorded in the following tables:—

Physical and Chemical Characteristics of Water-melon Oil

Specific Gravity	Saponification Value	Iodine Value	
At 20° C	Mgrms. KOH.	Per cent	Observer
0·9160 (water at 4° =1)	189·7	118	Wijs
0·9233 [2] (water at 20° =1)	191·8 ; [2] 189·9 [3]	121·1 ; [2] 121·8 [3]	Power and Salway
0·9219 [3]			

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point	Melting Point	Neutralisation Number	Saponification Value	Mean Molecular Weight	Iodine Value
°C	°C	Mgrms. KOH	Mgrms. KOH		Per cent
Titer Test. 32	34	197·1	197·1	284·1	122·7

The oil gives neither the *Halphen* nor the *Baudouin* reactions.

SENAT SEED OIL

Cucumis Chate, L., the senat plant grown in the Anglo-Egyptian Sudan as a cultivated plant (and also occurring widely as a weed), contains 30 to 38 per cent of a pale yellow oil, furnishing the following characteristics : [4]—

[1] *Zeits f. Unters d. Nahrgs- u. Genussm.*, 1903, 192.
[2] Expressed oil. [3] Extracted oil.
[4] *Bull. Imp. Inst.*, 1913, 56.

Oil—

Specific gravity at 15/15° C.	0 924
Saponification value	187-192
Iodine value	117-128·5

Fatty Acids—

Insoluble acids + unsaponifiable . . .	96·6
Titer test	30·3

MELON SEED OIL [1]

French—*Huile de melon, huile de petit béraff (béreff).*
German—*Melonenol.* Italian—*Olio di mellone.*

Physical and Chemical Characteristics of Melon Seed Oil

Solidifying Point. °C.	Melting Point °C.	Saponification Value	Iodine Value
5 5	5	193 3	101 5

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point. °C.	Melting Point. °C.
36	39

Melon oil is obtained from the seeds of *Cucumis melo,* L , which form an article of commerce on the Slave Coast and Gold Coast of West Africa. The seeds examined by *Fendler* contained 43·8 per cent of oil.

The specimen of oil examined had the acid value of 4·81.

Lidoff describes a melon seed oil obtained in the south of Russia by expression. The oil is used for edible purposes, but is not an article of commerce. The numbers obtained by *Lidoff* deviate so much from those given for both water-melon oil and melon seed oil that they have not been admitted into the tables. His results are as follows :—

Yield of oil by extraction . . .	29·4 per cent
Specific gravity of the oil at 15·25° C. .	0 9276
Saponification value	190·5
Iodine value	133·3
Percentage of insoluble acids + unsaponifiable matter	95 3 per cent
Iodine value of the fatty acids . .	128
Viscosity at 70° C, in Engler's apparatus (water=1)	8·9
Acid value of the sample . . .	1·37

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.,* 1903, 1025.

Lidoff also found a high acetyl value. His conclusion, that the proportion of hydroxy acids in the oil is large, must be accepted with reserve (cp. Vol. I. Chap. VI.).

The oil from the seeds of Indian *Cucumis sativus* (*Hooper* [1]) has the following characteristics :—

Oil—

Specific gravity at 15° C	0.924 ; 0.923
Saponification value	195.2 ; 196.9
Iodine value	117.6 ; 118.5
Reichert-Meissl value	0.52

Fatty Acids—

Insoluble acids + unsaponifiable	94.2 ; 94.6
Titer test	35.5° C.
Acid value of the specimen examined	11.5

MAIZE OIL, CORN OIL

French— *Huile de maïs.*   German— *Maisöl.*   Italian— *Olio de maïs. Olio di granturco.*

For tables of characteristics see pp. 169, 170.

The germs of the maize plant, *Zea Mays*, L., from which this oil is obtained, are recovered, in the process of manufacturing starch, by sifting and winnowing from the starch granules in which they are imbedded. The oil is therefore a by-product of starch and glucose works using maize (" corn ") as their raw material.

Formerly maize oil was obtained as a by-product in the alcohol distilleries. When the malted and crushed grain was allowed to ferment, the oil was laid bare and rose to the top in the fermentation vats. Before distilling off the alcohol, the oil was ladled off and purified in a crude fashion by washing, filtering, and " settling." Since, however, the presence of the germ imparts an unpleasant flavour to the spirit obtained by fermentation, and the oil so recovered was very impure, and had a different character from oil expressed from the germs, the older process of fermenting the crushed grain has been abandoned. At present the " corn " is first malted, then crushed, beaten up with water to a fine pulp, and the germ separated from the starch by sieving. The isolated germs are then expressed like oleaginous seeds in hydraulic presses. In a dry condition the germs contain 53 per cent of oil, and yield in practice about 40 per cent.[2] The whole grain contains 4–10 per cent of oil. The cake, which results as a by-product in the expression of the germs, is sold as cattle food of somewhat inferior value.

At the St. Louis Exhibition, 1904, the author saw a collection (arranged by the State of Illinois), demonstrating experiments made at

[1] *Annual Report, Indian Museum*, 1907–1908, p. 13.
[2] T. B. Wagner, in the *Journ. Soc. Chem. Ind.*, 1909, 342, states that the germ contains 29·6 per cent.

the Agricultural Experiment Station of Illinois at Champaign, where
for a number of years it was attempted to produce two kinds of grain,
one containing a large percentage of oil, and a second containing small
percentages of oil The result of these experiments, which had been
protracted during seven generations of seeds, is shown in the following
table :—

Year.	Grains containing High Percentage of Oil	Grains containing Low Percentage of Oil
1896	4·70	4 70
1897	4 73	4 06
1898	5·15	3 99
1899	5 64	3 82
1900	6 10	3·95
1901	6 09	3 43
1902	6·41	3 01
1903	6 53	2 97

Maize oil, if properly prepared, is clear yellow in colour, and does
not require refining for commercial purposes. If, however, the oil is
badly prepared and allowed to stand in contact with albuminoid
matter so that it undergoes a process of fermentation, whereby con-
siderable quantities of free fatty acids are produced (see Vol. I. Chap.
I.), it acquires a dark colour and becomes unsuitable for light-coloured
soaps Such oil is therefore bleached in soap works in the same manner
as linseed oil (p. 59).

Freshly-prepared maize oil has a pale yellow or golden-yellow colour,
and a distinctive odour ; its taste is pleasant at first, and recalls that
of newly ground corn-meal. It is therefore possible to identify the oil
by its taste alone.

Fresh oil contains but small quantities of free fatty acids, whereas
the oil recovered by the older processes from the fermentation vats
was characterised by a large amount of free fatty acids The solubilities
of the oil in absolute alcohol, acetone, and glacial acetic acid, are collated
in the following table, due to *Smith* . [1]—

Solubility of Maize Oil in 100 volumes of				
Absolute Alcohol		Acetone, commercial	Glacial Acetic Acid	
At 16° C	At 63° C.	At 16° C.	At 16° C	At 63° C.
2	13	24	3	9

Maize oil is characterised by its high amount of unsaponifiable
matter. *Spüller* [2] obtained 1·35 per cent, and *Hart* [3] 1·55 per cent.

[1] *Journ. Soc. Chem. Ind.*, 1892, 505   [2] *Dingl. Polyt. Journ.*, 264, 626
[3] *Journ. Soc. Chem. Ind.*, 1894, 257.

of unsaponifiable matter. *Hopkins* found in a specimen of maize oil 1·49 per cent of lecithin and 1·37 per cent of phytosterol. A sample of maize oil examined in the author's laboratory gave even 2·32 per cent of unsaponifiable matter.

The " unsaponifiable " consists of lecithin, and of an alcohol which was looked upon by earlier observers (*Hoppe-Seyler, Hopkins*) as cholesterol. Since, however, purified crystals obtained by *Gill and Tufts* [1] from about 4 kilos of maize oil melted at about 138°-138·3° C., and its acetate at 127·1° C., the alcohol must be sitosterol. *Konig and Schluckebier* [2] repeatedly recrystallised maize oil " phytosterol " and obtained in the sixth, seventh, eighth, and ninth successive crops crystals of the melting points 139·6°, 140·8°, 140·4°, and 140·4° C. respectively. The last crop of crystals gave an acetate melting at 135·8° C., and after the third crystallisation at 137° C.

In the elaidin test, maize oil, like cotton seed oil, yields a mass of buttery or pasty consistence. The viscosity of maize oil has been stated by *Winfield* to be at 20° C. 9·79-10·7 times that of water. Taking the viscosity of rape oil at 100, the viscosity of maize oil works out at 70·4-70·65.

The saturated fatty acids in maize oil amount, according to *Hopkins*, to 4·55 per cent ; *Tolman and Munson*, however, obtained 7·44 per cent of solid fatty acids by the lead-salt-ether method. Hence, *Vulté and Gibson's* statement that the mixed fatty acids consist of 27·74 per cent solid fatty acids and 72·26 per cent liquid fatty acids, can only be explained by the fact that the solid acids had not been completely exhausted with ether. This is confirmed by the further statement that the separated solid fatty acids still absorbed 54·23 per cent of iodine.

According to *Vulté and Gibson* the solid fatty acids consist of palmitic, stearic, and arachidic acids, but considering that *Hehner and Mitchell* found no stearic acid in maize oil, this statement stands in need of confirmation. Linoleic acid seems to be absent, since no ether-insoluble brominated glycerides could be obtained ; nor did *Hopkins* [3] find any linusic acid amongst the products of oxidation. The liquid fatty acids contain considerable proportions of linolic acid (*Lewkowitsch*, see Vol. I. Chap. VIII. p. 563). The liquid fatty acids may be considered as consisting of a mixture of linolic and oleic acids. Small quantities of volatile fatty acids used to occur in commercial oils, as was evidenced by the high *Reichert* values of specimens obtained from fermentation processes. At present, however, the commercial maize oils being prepared exclusively by the modern process are devoid of volatile acids.[4] The high acetyl value *Lewkowitsch* found, viz. 7·8-8·75, was due to the same cause, although to some extent at least the large amount of unsaponifiable matter may account for it.

[1] *Journ. Amer. Chem. Soc.*, 1903, 251.
[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908 (xv.), 652.
[3] *Journ. Amer. Chem. Soc.*, 1809, 948.
[4] One sample of " distillery oil " stated to have yielded 88·21 per cent insoluble acids + unsaponifiable, had the high Reichert value of 9·9.

Physical and Chemical Characteristics of Maize Oil

Specific Gravity			Solidifying Point		Saponification Value			Iodine Value	
At °C		Observer	°C	Observer	Mgrms KOH	Observer		Per cent	Observer
15	0·9215- 0·9220	De Negri and Fabris	−10 to −15	De Negri and Fabris Hopkins	190·4	De Negri and Fabris		121-130·8	Lewkowitsch
15·5	0·9274	Lewkowitsch	−36	Lewkowitsch	191·9	Lewkowitsch			
,,	0·9243	Archbutt	"stearine" deposits at the ordinary temperature on standing		189·7	Archbutt			
,,	0·9213·	Winfield			192·6	Winfield			
,,	0·9255								
100	0·8711- 0·8756	,,							

Physical and Chemical Characteristics of Maize Oil—continued

Refractive Index		Maumené Test		Thermal Tests	
At 15° C	Observer	°C	Observer	Heat of Bromination °C	Observer
1·4768	Tolman and Munson	86	De Negri and Fabris	21·5	Hehner and Mitchell
Butyro-refractometer		79	Jean[1]		
Degrees at 15° C	Observer	81·6	Archbutt		
77·5	Tolman and Munson				

[1] By Jean's method.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer	°C.		Observer.	°C.	Observer.	°C.	Observer	Mgrms KOH.	Observer	Per cent	Observer.
95·7 93·57	Hart Hopkins	100	0·8529	Winfield	16·14	De Negri and Fabris	18·20 21·6	De Negri and Fabris Tolman and Munson	198·4	Spuller	125 113·115	Spuller De Negri and Fabris
						Test Test					*Iodine Value of the Liquid Fatty Acids*	
					19	Lewkowitsch					140·7	Wallenstein and Finck
											142·2-143·7[1]	Tortelli and Ruggeri

[1] From an oil having the iodine value 123·3-124·6.

Maize oil is a representative type of a semi-drying oil ; it has somewhat better drying powers than cotton seed oil, but differs from the latter in that it is not oxidised with equal energy, when finely subdivided on cotton waste, although it " heats " with sufficient rapidity to render it dangerous as a lubricating oil (cp. Vol. III. Chap. XV.). In the *Livache* test two samples of maize oil of different origin gained 5·97 and 5·19 per cent in seven and ten days respectively.[1]

No decided drying properties are imparted to maize oil by subjecting it to the process of " boiling," or by the addition of driers If, however, a current of air is passed through the oil at 150° C., it acquires, on addition of manganese borate, some drying properties, and a thin film of the oil so treated spread on lead dries in from ten to twenty hours to a viscous mass.

When cotton seed oil is lower in price than maize oil, the latter is extensively adulterated with cotton seed oil. Although it is easy to differentiate pure maize oil from pure cotton seed oil, the detection of a small proportion of maize oil in cotton seed oil by chemical tests is at present impossible. *Gill and Tufts* are of the opinion that it may be feasible to detect cotton seed oil in maize oil by the melting point of the acetate of the alcohol isolated from the unsaponifiable matter. From pure cotton seed oil, after recrystallising the acetate six times, crystals of the melting point 120°-121° C. were obtained from a mixture of 90 per cent of cotton seed oil and 10 per cent of maize oil crystals melting at 121 5°-122 5° C., and from a mixture of 80 per cent of cotton seed oil and 20 per cent of maize oil crystals melting at 121°-125° C., whereas crystals from pure maize oil melted at 127·1° C. Since, however, *Bömer and Winter* obtained sitosteryl (phytosteryl) acetate melting at 123°-124° C. from cotton seed oil, further confirmation of the reliability of the " sitosterol test " is required. In the present state of our knowledge the *Halphen* colour test (in which the colour of maize oil remains unchanged) and a higher titer test of the fatty acids than 20° C., must be relied upon as indicating the presence of cotton seed oil.

Well-refined maize oil is used for edible purposes (salad oil). Since its " grainy " taste is objectionable, the edible quality is mostly mixed with edible cotton oil and other edible oils Maize oil is also used in the manufacture of margarine—" oleo-margarine " of the United States—as also in the manufacture of compound lard (replacing cotton seed oil). Such maize oil as cannot be employed for edible purposes is used chiefly in making soft soap, for which it is eminently suitable. A cotton " softener " largely used in the United States contains maize oil soft soap. For hard soaps of acceptable quality maize oil is not suitable.   •

The maize industry has assumed enormous dimensions in the United States on account of the extensive manufacture of glucose ; consequently the amount of maize oil, which is the by-product of this industry, has also reached enormous quantities.[2]   Very large amounts of maize

[1] H. Winfield, *Inaug. Dissert.*, New York, 1899.

[2] Cp. T. B. Wagner, "The American Industry of Corn Products," *Journ. Soc. Chem. Ind.*, 1909, 342 ; also W. P. Kaufmann, " Maize Products, and Maize Starch and its Products," *Journ. Soc. Chem. Ind.*, 1910, 527.

oil are also imported from the Argentine and are beginning to come in from the south of Africa. Large quantities of maize reach this country for brewing purposes ; maize oil is recovered therefrom in not inconsiderable quantities as a by-product, although a great portion of the germs is sold as cattle food.

To indicate the extent to which maize oil has been employed in Europe for soap-making, the following statistical data may be quoted :—

Corn Oil—Exports from the United States of America, 1902–1912

Year	Gallons	Value Dollars
1902	4,266,398	1,769,370
1903	3,778,035	1,167,493
1904	3,222,875	998,613
1905	3,108,917	890,937
1906	3,833,251	1,172,206
1907	3,568,571	1,411,556
1908	2,717,804	1,052,310
1909	2,656,703	1,293,580
1910	1,228,188	643,392
1911	2,751,825	1,573,695
1912	2,594,116	1,526,931

(It is noteworthy that in consequence of the lower prices of cotton oil ruling in the years 1902 and 1903, the import of maize oil into this country almost ceased in those years.) Lower qualities are used as a burning oil. The oil has also been recommended for lubricating, but on account of its gumming properties it cannot be usefully employed for this purpose. Notwithstanding many statements to the contrary, maize oil cannot be used as a paint oil on account of the poor drying properties which paints prepared with this oil possess. It found, however, extensive employment in the United States for the manufacture of vulcanised maize oil, before soya bean oil took its place.

TOMATO SEED OIL

French—*Huile de tomate.* German—*Tomatosamenol.*
Italian—*Olio di pomodoro.*

In view of the large quantities of tomato seeds (from *Lycopersicum esculentum*, Mull) obtainable as a by-product in the manufacture of tomato pulp, it is not unlikely that the preparation of this oil will be undertaken commercially in Italy. Thus in the province of Parma alone 13,000 tons of tomatoes were treated in 1908,[1] yielding about 3000 tons of seeds containing 18 per cent of oil. Indeed, several proposals have been made to that effect.

[1] P. Accomazzo, *L'Industria chimica*, 1910, 360.

The following characteristics were ascertained by *Battaglia* [1] and by *J. Kochs* : [2]— .

	Kochs	Battaglia
Oil—		
Specific gravity	0·920	0·922
Solidifying point	below −12° C.	..
Saponification value	183 6	190·4
Iodine value	117·8	106 9
Reichert-Meissl value	0 22	..
Unsaponifiable	2 68 per cent	..
Butyro-refractometer "degrees" at 40° C.	63	..
Fatty Acids—		
Insoluble fatty acids + unsaponifiable .	..	95 1
Melting point (capillary tube) . . .	26° to 29° C.	..
Neutralisation value	199 5	..
Iodine value	129 6	112 0
Refractive index	..	1 473

Battaglia identified amongst the fatty acids, myristic, stearic, oleic, and linolic acids.

<div align="center">

PERSIMMON SEED OIL [3]

</div>

French—*Huile de plaqueminier de Virginie.* German— *Dattelpflaumenol.*
Italian—*Olio di diospiro*

For tables of characteristics see p. 174.

This oil is obtained from the seed of *Diospyros virginiana,* L [4] It has a brownish-yellow colour ; its taste and smell recall that of arachis oil produced by expression in the hot.

The oil contains 9·11 per cent of solid acids of the mean molecular weight 298, and 85 5 per cent of liquid acids of the mean molecular weight 285. No arachidic acid could be detected amongst the solid acids.

[1]. *Les Corps gras,* 1901, 135.
[2] *Jahresb. d. Versuchs d. k Gartenlehranst. far 1906–1907,* Dahlem.
[3] N. J. Lane, *Journ. Soc. Chem Ind,* 1905, 390
[4] With regard to studies on the ripening of persimmons from the Virginian and Japanese species (*Diospyros Kaki*) cp. Bigelow, Gore and Howard, *Journ. Amer. Chem. Soc.,* 1906 (28), 688.

Physical and Chemical Characteristics of Persimmon Seed Oil

Specific Gravity	Solidifying Point	Melting Point.	Saponification Value	Iodine Value
At 15° C.	° C.	° C.	Mgrms. KOH	Per cent.
0.92437	−11	−6	188	116.8

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.	Specific Gravity	Solidifying Point	Melting Point	Neutralisation Value	Mean Molecular Weight	Iodine Value of Liquid Fatty Acids
Per cent	At 15° C	° C.	° C.	Mgrms. KOH		
95·9	0.9043	20.2 (Titer Test)	20·2	192.7	291.5	134-135

WHEAT OIL

French—*Huile de blé.*   German—*Weizenkernol.*
Italian—*Olio di germi di grano.*

For tables of characteristics see p. 175.

Wheat oil is contained in the germs of the wheat grains to the extent of 12·5-17·5 per cent (1 to 1·8 per cent of the whole grain). One ton of germs yields about 280 lbs. of oil.[1]

In the fresh state the oil is pale yellow and has the characteristic odour of wheat meal. It is insoluble in absolute alcohol in the cold, but dissolves in 30 parts of hot absolute alcohol. At 65° C. it is soluble in an equal volume of glacial acetic acid

The oil easily turns rancid (most likely owing to the presence of an enzyme; cp. "Rice Oil") and thereby becomes dark brown. A freshly extracted specimen contained 5·65 per cent of free fatty acids (calculated to oleic acid); after one year the same sample contained 43·86 per cent. Oils from different kinds of germs behave differently (cp. the numbers given in the tables).

The specimen examined by *Frankforter and Harding* contained 2 per cent of lecithin and 2·5 per cent of sitosterol. The high percentage of both lecithin and alcohol shows the relationship of this oil to maize oil.

This oil is not identical with wheat-meal oil (cp. p. 293).

[1] *Chem. Revue,* 1904, 128.

Physical and Chemical Characteristics of Wheat Oil

Specific Gravity		Solidifying Point.		Saponification Value.		Iodine Value		Refractive Index.			
At ° C.	Observer.	° C.	Observer.	Mgrms. KOH	Observer.	Per cent.	Observer.	At ° C.			Observer.
15	0·9245	15	De Negri	182·81	De Negri	117·2	De Negri	20	1·4825		Frankforter
„	0·9292-	Semi-solid	Frankforter	1874-190·3	Frankforter	115·6	Frankforter	30	1·47936		and
	0·9374	at 0	and		and		and	40	1·47447		Harding
	De Negri[1]		Harding		Harding		Harding				
	Frankforter								Butyro-refractometer		
	and								"Degrees"		
	Harding[2]								74·5		De Negri

[1] *Journ. Soc. Chem. Ind.,*1895, 1155. [2] *Ibid.,*1899, 1030.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point		Melting Point.		Iodine Value	
° C	Observer	° C	Observer.	Per cent	Observer.
24·7	De Negri	39·5	De Negri	123·27	De Negri

DATURA OIL, THORN APPLE SEED OIL

French—*Huile de datura.* German—*Stechapfelol, Daturaol.*
Italian—*Olio di stramonio.*

The air-dried seeds of *Datura Stramonium*, L. (thorn apple), contain a fatty oil, which occurs therein to an extent of 25 per cent (*Cloez*); 16·7 per cent (*Holde*); 18·7 per cent (*Meyer and Beer*).

The oil prepared by *H. Meyer and R. Beer* has a light yellow-greenish colour and a characteristic smell. At 20° C. it thickens without, however, solidifying. After standing for a prolonged time in the cold a small amount of "stearine" melting at 60° C. separated out. The acid value of the specimen examined by *H. Meyer and R. Beer* was 8·1.

Gérard first isolated from this oil (margaric) daturic acid, $C_{17}H_{34}O_2$, and although its existence was doubted [1] and it was looked upon as a mixture [2] of acids of molecular weight from 280 to 291, its individuality and occurrence in datura oil has been placed beyond doubt by *Meyer and Beer*.[3]

The approximate composition of the fatty acids in datura oil is, according to these authors, as follows :—

Palmitic acid	.	.	.	.	.	10·0 per cent
Daturic acid	.	.	.	.	.	2·5 ,,
Oleic acid	.	.	.	.	.	62·0 ,,
Linolic acid	.	.	.	.	.	15 0 ,,

It would appear that small quantities of fatty acids of a molecular weight exceeding 320 are also present. Neither stearic acid nor linolenic acid nor any volatile acids could be detected. The oil contains further 1·01 per cent of unsaponifiable matter, yielding a phytosterol melting after recrystallisation at 128° C.

When heated to 50° C. in a thin layer for thirteen hours, the oil forms a firm skin; at the ordinary temperature it only begins to show signs of drying after 35 days.

The viscosity of the oil in *Engler's* viscosimeter is 9 compared with water at 20° C.

Physical and Chemical Characteristics of Datura Oil

Specific Gravity at 15° C.	Solidifying Point	Saponification Value Mgrms. KOH	Iodine Value Per cent	Observer
0 9228	..	..	..	Cloez [4]
0·9175	thickens at − 15°	186	113	Holde
0·923	,, − 12°	202	113·2	Meyer and Beer

[1] Holde, *Mitt. d. Konigl. Tech. Versuchs.*, 1902, 20 (2), 66. Cp. also *Ibid.*, 1903, 59.
[2] *Berichte*, 1905, 1252. [3] *Monatsh. f. Chem.*, 1910 (31), 1239.
[4] *Ann. de chim. et de phys.*, 1892 (27), 551.

The oil from *Datura metel* which furnishes the "metel nuts," known to the natives of East Africa for their medicinal properties,[1] has been described by *F. Suzzi*.[2] The seeds contain 15·27 per cent of a pale yellow oil having a peculiar odour and an unpleasant taste. *Suzzi* gives the following characteristics :—

Oil—

Specific gravity at 15° C.	0·9225
Solidifying point	12-15° C.
Saponification value	198·4
Iodine value	116·2
Maumené test	74·8° C.

Fatty Acids—

Solidifying point (titer test).	22·3° C.
Neutralisation value .	195·1
Saponification value .	196
Mean molecular weight	286·2

The oil gives neither the *Halphen* nor the *Baudouin* test. It is used as a burning oil in Erythrea (Italian East Africa).

<div align="center">BEECHNUT OIL</div>

<div align="center">French—<i>Huile de faîne</i>.   German—<i>Buchekernöl</i>.
Italian—<i>Olio di faggio</i>.</div>

For tables of characteristics see p. 178.

Beechnut oil is obtained from the fruit of the red beech-tree, *Fagus sylvatica*, L. The fruit consists of 33 per cent of husks and 67 per cent of kernels ; the latter contain 43 per cent of oil. The oil is prepared in small installations on the Continent, as obviously it cannot be obtained in large quantities. (A patent[3] was taken out in this country as early as 1713 for the manufacture of beechnut oil, but at present the oil is not produced in this country.) The cold-drawn oil obtained from the shelled kernels is of pale yellow colour and free from unpleasant taste. This quality of oil is used for culinary purposes, whereas that expressed at a higher temperature is employed as burning oil.

Beechnut oil is stated to be used as an adulterant of almond oil ; its presence may be detected by determining the *iodine value* of the sample.

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[1] The seeds contain hyoscyamine and scopolamine (E. Schmidt, *Arch. d. Pharm.*, 1910 (248), 641.

[2] *I Semi oleosi e gli oli.* Published for the Milan Exhibition, 1906.

[3] Aaron Hill, English patent 393, 1713.

Physical and Chemical Characteristics of Beechnut Oil

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Maumené Test		Refractive Index. Oleo refractometer	
At 15° C	Observer	°C	Observer	Mgms KOH	Observer	Per cent	Observer	°C	Observer	"Degrees" at 25° C	Observer
0·9225	Schübler	−17	Chateau	196·3	Girard	111·2	De Negri and Fabris	65	Maumené	+16 5 to +18	Jean
0 9205	Masse			191·1	De Negri and Fabris	120 1	Wijs	63	De Negri and Fabris		
0 9220	De Negri and Fabris										

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value.	
Per cent	Observer	°C	Observer	°C	Observer	Per cent	Observer
95 16	Girard	17	Girard	24	Girard	114	De Negri and Fabris
				23	De Negri and Fabris		

KAPOK OIL

French—*Huile de kapock ; huile de capoquier.* German—*Kapokol.*
Italian—*Olio di kapok.*

For tables of characteristics see p. 180.

Kapok oil is obtained by expressing the seeds of *Eriodendron anfractuosum*, D.C.(=*Bombax pentandrum*, L.), and *Bombax Ceiba* (=*Bombax malabaricum*, D.C.). Both trees are indigenous to the tropics. *E. anfractuosum* grows in great profusion in the East and West Indies, the Malayan Archipelago, Indo-China (Cochin-China and Cambodja), Mexico, the Antilles, Guiana, and Africa (Madagascar, Senegal, Ivory Coast, Dahomey, Nigeria).[1] In Nigeria the 'tree is known as " cotton tree " and " silk cotton tree." The seeds are of the size of peas ; they are enclosed in a hard black shell, forming about 40 per cent of the seeds. The plant is related to the cotton plant , the hairs covering the fruit resemble cotton, although they have neither the strength nor the staple of the latter.[2] Kapok hair is used as a substitute for horse-hair in upholstery (for filling mattresses, cushions, life-belts, etc.).

The seeds are free from hairs, hence they do not offer the same difficulty which cotton seed presents to the seed-crusher. A light crushing between rollers and winnowing through sieves, assisted by a current of air, separates the husk from the kernel. The seeds have the following average composition :—

Oil .	.	.	.	.	24·20	per cent
Water	.	.	.	.	11 85	,,
Ash .		.	.	.	5 22	,,
Crude fibre .			.	.	23 91	.,
Albuminoids	.		.	.	18 92	,,
Carbohydrates, etc.		.	.	.	15 90	,,

Kapok seed is expressed on a commercial scale in Holland ; the yield of the oil from the whole seed is 17·8 per cent on a manufacturing scale.

The oil has a greenish-yellow colour and a not unpleasant taste and odour.

The numbers given in the table of characteristics in the last edition of this work [3] show very great differences, especially as regards the saponification and iodine values. The *Reichert* value as also the Acetyl value given by *Philippe* appear so extraordinary that the author considered it best to ignore them in this present table of characteristics. Renewed examination of the oil is desirable.

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[1] Cp. M. Mueke, *Der Pflanzer*, 1908, 290, 305 , "Kapok and its Cultivation," *Bull. Imp. Inst.*, 1911, 121.

[2] *Journ. Soc. Arts*, 1893, 1030 ; *Journ. Soc. Chem Ind.*, 1894, 147.

[3] Vol. II. p. 142.

Physical and Chemical Characteristics of Kapok Oil

	Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Maumené Test		Refractive Index Oleo-refractometer at 40° C.	
At C°	Observer		C	Observer	Mgms KOH	Observer	Per cent	Observer	C	Observer	Degrees	Observer
18	Henriques				181	Henriques Philippe	117	Henriques	56	Henriques		
100	Durand and Baud, Spunk-meyer	28 0	Durand and Baud	196 5 26 0	Durand and Baud	119	Durand and Baud (4)			51 3	Durand and Baud Spunk-meyer
15					189 2 194 5	Spunk-meyer	87 21 93 78				51 7 50 1	

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Specific Gravity		Solidifying Point		Melting Point		Neutralisation Value		Mean Molecular Weight		Iodine Value	
Per cent	Observer.	At C°	Observer	C	Observer	C	Observer	Mgms KOH	Observer		Observer	Per cent	Observer
94 5 — Philippe	Henriques	18	0 902	Henriques	23 24 41 5 32	Henriques Philippe Durand and Baud	30 35 5 36	Henriques Philippe	211 209	Philippe	203	Henriques	108 122 5	Henriques (4)
95 96	Spunk-meyer				29 0 31 8	Spunk-meyer	32 2 34 3	Spunk-meyer	196 0 202 7	Spunk-meyer			84 8 98 9	Spunk-meyer

The mixed fatty acids consist, according to *Philippe*, of 30 per cent of solid fatty acids, and 70 per cent of liquid fatty acids (determined by the lead-salt-ether method). The solid acids consist exclusively of palmitic acid. On standing, kapok oil, like cotton seed oil, deposits "stearine." The great resemblance of kapok oil to cotton seed oil is further accentuated by the great similarity of the colour reactions of the two oils. Thus kapok oil gives with nitric acid a similar reaction to that which cotton seed oil shows; in the case of kapok oil the tint is stated to be more greenish-brown than reddish-brown. The most characteristic colour reaction of cotton seed oil—the *Halphen* test—is also given by kapok oil. This fact deserves attention on the part of the analyst. It should, however, be distinctly noted that a sample of kapok oil extracted by the author from genuine seeds of *Eriodendron anfractuosum* did not exhibit the *Halphen* reaction. Perhaps this may be due to the oil having stood before testing about thirteen months.

Kapok oil is used in its home for edible purposes. Seeds imported from Java are crushed in Holland, and the oil is used for soap-making as a substitute for cotton seed oil. Attempts have been made in Marseilles to crush Kapok seed.

The oil is easily saponified and is thrown out of the paste by salt solution.[1]

COTTON SEED OIL

French—*Huile de coton.*   German—*Baumwollsamenol, Cottonol.*
Italian—*Olio di cotone.*

For tables of characteristics see pp. 188-190.

Cotton seed oil is expressed on a very large scale from the seeds of the various kinds of the cotton tree, *Gossypium*. The species cultivated extensively in the United States is *Gossypium hirsutum*, L. ("Upland cotton" covered with "linters"), whereas the plant grown in the Sea Islands and in Egypt is *Gossypium barbadense*, L. During the last decade East India (Bombay) seed, as also Levantine (Smyrna, Mersyne, Alexandretta), Brazilian[2] (Maranhao, Savanilla, Pernambuco), Peruvian (Payta), Russian (Samarkand, Ferghana),[3] and West African (Nigeria) seed has come into the European markets. The Indian species are generally assumed to be *G. neglectum* and *G. arboreum*, but it should be pointed out that they are not well defined.

[1] Cp. E. Boutoux, *Matières grasses*, 1910, 1828.
[2] Cotton in Brazil is chiefly grown in the *Northern States*—Pernambuco, Ceara, Seigpe, Maraukao, Rio Grande de Norte; *Middle States*—San Paulo, Minas Geraes, Rio de Janeiro.
[3] In the Ferghana district the production of cotton seed oil has reached the dimensions of a considerable industry. In the year 1902 there were already six seed-crushing mills. In the year 1908 there were opened five more oil mills, intended to produce about 25 tons of oil per day. In 1911 there were in active operation 30 mills (see p. 192). Cotton cake is exported from Russia to the continent of Europe.

Physical and Chemical Characteristics of Kapok Oil

	Specific Gravity		Solidifying Point		Saponification Value			Iodine Value		Maumené Test		Refractive Index Oleo-refractometer at 40° C.	
At C°	Observer		C	Observer	Mgms KOH	Observer	Per cent	Observer	C	Observer	Degrees	Observer
18	0·900	Henriques			181	Henriques Philippe	117·4	Henriques	96	Henriques		
100	0·803	Durand and Baud	25·0	Durand and Baud	196·5 26·0	Durand and Baud	119·5	Durand and Baud (4)			51·3	Durand and Baud Spunk- meyer
15	0·923 0·925	Spunk- meyer 6			195·2 194·5	Spunk- meyer	87·21 93·78				51·7 50·1	

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Acids + Unsaponifiable Per cent	Specific Gravity			Solidifying Point		Melting Point		Neutralisation Value		Mean Molecular Weight		Iodine Value	
	Observer	At C°	18	Observer	C	Observer	C	Observer	Mgms KOH	Observer		Observer		Observer
94·7 95·4	Henriques Philippe		0·902	Henriques	23-24 41·5 32	Henriques Philippe Durand and Baud	30 35·5 36	Henriques Philippe	191 199	Henriques Philippe (4)	268	Henriques	108 122·5	Henriques (4)
95·6	Spunk- meyer				30·5 31·8	Spunk- meyer	32·2 34·2	Spunk- meyer	199·0 202·7	Spunk- meyer		Spunk- meyer	86·8 98·9	Spunk- meyer

1 Moisture 8·4, nitrogen 1·94, 1·96, 5, 32 (the oil was obtained by cold pressing). 2 By Archbutt's process. 3 fresh. 5 e Chem Ind. 1904, 278. 4 there air dry. 5 1904, 5, 32 (the oil was extracted with ether). 6 From Baumé analyses, Zsch. f. Nahrgs u Genussm, 1913 (26) 88.

Year ended June 30.	Cotton Seed Crop.	Seed exported	Seed worked up	Oil produced.	Oil-cake¹ and Meal produced.	Oil exported.	Oil retained for Home Consumption.
	Tons	Tons	Tons	Gallons	Tons	Gallons	Gallons
1872	1,317,637	3,180	52,705	2,105,000	18,400	547,165	1,560,835
1873	1,745,445	3,003	52,354	2,094,000	18,300	709,576	1,384,424
1874	1,881,632	3,152	74,066	2,963,000	25,900	782,067	2,180,933
1875	1,688,516	2,638	84,325	3,373,000	29,500	417,387	2,955,613
1876	2,056,946	2,582	123,404	4,936,000	43,200	281,054	4,654,946
1877	1,968,590	3,155	134,429	5,137,000	34,400	1,705,422	2,231,578
1878	2,148,239	8,370	150,376	6,015,000	52,600	4,092,349	1,922,636
1879	2,268,117	8,199	181,451	7,258,000	63,500	4,352,530	1,905,470
1880	2,615,608	6,071	235,404	9,416,000	82,400	6,977,796	2,418,204
1881	3,038,695	5,814	182,321	7,293,000	63,800	3,444,084	3,848,910
1882	2,455,221	5,951	294,626	11,785,000	103,100	713,519	11,071,451
1883	3,266,385	5,900	391,966	15,679,000	137,200	415,611	15,263,389
1884	2,649,498	2,837	395,924	15,837,000	138,500	3,605,946	12,231,054
1885	2,624,835	5,524	495,718	19,449,000	174,500	6,364,279	13,584,721
1886	3,041,544	3,897	578,463	23,138,000	202,400	6,240,139	16,897,861
1887	3,018,360	6,616	694,222	27,769,000	243,000	4,067,138	23,701,862
1888	3,290,871	8,109	822,717	32,909,000	287,900	4,458,597	28,450,403
1889	3,309,564	5,687	794,295	31,772,000	278,000	2,690,700	29,081,300
1890	3,494,811	5,830	873,702	34,948,000	305,800	13,384,385	21,563,615
1891	4,992,678	5,045	1,023,169	40,927,000	358,100	11,003,160	29,923,840
1892	4,273,734	6,075	1,068,433	42,737,000	374,000	13,859,278	28,877,722
1893	3,682,673	2,760	1,050,282	42,011,000	367,600	9,462,074	32,548,926
1894	3,128,673	2,560	1,431,445	57,258,000	501,000	14,958,309	42,299,691
1895	4,759,205	2,526	1,434,511	57,390,340	502,044	21,187,228	45,903,112
1896	3,415,842	18,490	1,434,653	57,361,629	502,128	19,195,882	37,940,272
1897	4,070,100	13,283	1,628,040	65,122,600	569,300	27,108,884	37,013,118
1898	5,252,767	16,382	2,101,106	84,044,000	735,300	40,513,784	43,483,116
1899	5,471,521	17,222	2,352,754	94,110,900	823,400	50,627,219	43,482,781
1900	4,668,346	24,928	2,479,386	93,325,729	854,331	46,902,390	46,423,339
1901	4,830,280	21,665	2,415,140	96,605,600	845,299	49,356,741	47,248,859
1902	4,983,239	25,202	2,975,000	119,000,000	1,041,250	23,042,848	85,957,152
1903	5,208,000	25,811	3,277,233	122,908,158	1,165,339	35,642,994	87,265,164
1904	4,716,591	10,551	3,241,428	121,877,618	1,155,568	29,014,417	92,863,875
1905	6,426,698	11,859	3,345,370	133,817,772	1,360,172	53,345,580	82,282,192
1906	5,060,205	8,814	3,731,175	125,700,928	1,271,740	43,793,519	81,907,409
1907	5,912,646	14,239	3,843,981	153,760,000	1,785,594	41,880,304	133,844,536
1908	4,952,402		2,564,873	103,043,820	1,043,080	41,929,991	
1909	5,903,588		3,669,747	146,788,880	1,491,752	23,550,468	
1910	4,462,000		3,263,000	131,000,000	1,326,000		
1911	5,175,000		4,106,000	164,970,000	1,792,000		

¹ Exports of oil-cake since 1895 have been as follows (in tons of 2000 pounds), 1895, 241,875 tons; 1896, 364,468 tons; 1897, 311,018 tons; 1898, 470,863 tons,
1899, 539,996 tons; 1900, 571,852 tons; 1901, 629,343 tons; 1902, 526,238 tons; 1903, 540,399 tons; 1904, 410,175 tons; 1905, 425,074 tons; 1906, 545,417 tons;
1907, 670,484 tons.

² Of these there were taken by: Holland, 6,630,227; France 5,145,565; Germany, 4,465,121; Mexico, 3,994,849; Great Britain, 2,422,118; Italy, 2,221,140

The following table gives the results of the official census, published by the United States Government :—

	Census.		
	1909.	1904.	1899.
Number of active establishments	809	717	357
Seed, crushed :—			
Quantity, tons	3,827,300	3,345,400	2,479,400
Cost	$78,112,000	$51,879,000	$28,633,000
Average cost per ton	$20·41	$15·51	$11·55
Average crush per establishment, tons	4,734	4,666	6,945
Crude products :—			
Total value	$107,538,000	$69,311,000	$42,442,000
Average value per establishment	$133,000	$97,000	$119,000
Oil—			
Quantity, gallons	158,328,500	133,817,800	93,325,700
Value	$55,328,000	$31,342,000	$21,391,000
Average value per gallon	$0·35	$0·23	$0·23
Meal and cake—			
Quantity, tons	1,674,500	1,360,000	884,400
Value	$40,193,000	$27,767,000	$16,031,000
Average value per ton	$24·18	$20·42	$18·13
Hulls —			
Quantity, tons	1,269,200	1,213,000	1,169,200
Value	$7,711,000	$5,589,000	3,189,000
Average value per ton	$6·08	$4·61	$2·73
Linters —			
Quantity, pounds	175,512,100	117,793,000	57,272,000
Value	$4,006,000	$4,613,000	$1,801,000
Average value per pound	$0·023	$0·039	$0·031

It will be seen that the figures given in this table are not identical with those given in table, p. 183, this is partly due to the fact that the foregoing table refers to the years ending December.

The several States in which cotton seed oil is grown and crushed are, arranged in the order of their production, the following :—Texas, Georgia, Mississippi, Louisiana, Arkansas, South Carolina, Tennessee, North Carolina, Alabama, Indian Territory, Oklahoma, Missouri, Florida.   All the other States together produce less than Florida, whose production is quite insignificant compared with that of Texas.

Comparatively small quantities of American seed are exported, as may be gathered from the table, which states the quantities of cotton seed imported by the United Kingdom during the last ten years :—

Cotton Seed imported by the United Kingdom

From	1902	1903	1904	1905	1906	1907	1908	1909	1910	1911
	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons
France	1,473	712	2,220	978	871	56	209	16	174	26
Germany	62	476	1,520	1,917	2,314	925	934	1,008	200	822
Turkey	12,168	2,381	6,480	8,906	13,753	9,813	18,068	17,809	6,397	9,194
Egypt	374,024	313,350	319,077	385,615	362,592	407,797	376,118	331,608	190,609	208,359
United States of America	21,241	15,127	4,710	4,132	3,007	1,865	1,048	5,751	1,012	5,830
Republic of Colombia	501	302	229	129	193	698	184	736	573	870
Peru	2,836	2,910	2,137	3,013	3,334	5,088	11,344	9,895	8,458	7,938
Chile	768	685	523	622	1,328	576	525	430	447	252
Brazil	24,061	23,692	18,893	35,092	28,116	28,046	25,742	31,745	20,913	35,826
Other foreign countries	984	332	7,604	3,789	2,344	1,435	2,222	2,639	1,388	1,412
British East Indies	111,814	176,085	104,230	123,342	202,790	279,288	155,350	177,088	415,192	197,773
Cyprus							131	1,002	102	104
Southern Nigeria							2,260	4,178	1,662	1,631
Northern Nigeria										
British West Indies							1,616	721	283	748
Other British possessions	688	839	1,028	1,393	1,909[1]	830[2]	1,054	1,610	2,397	3,948
Russia					229	17,980	608	2,704	6,050	3,526
Portuguese East India						13,127	16,170	5,920	30,224	23,222
Hayti and San Domingo					504	3,253	2,672	2,913	3,284	4,889
Total	550,620	537,491	468,653	568,928	624,765	738,152	616,255	597,773	689,575	546,370

[1] 400 tons from British West India Islands   [2] 514 tons from British West India Islands.

The bulk of the Egyptian cotton seed comes to England. Thus out of 457,766 tons shipped from 1st September 1906 to 31st August 1907, 382,542.tons were sent to England. The quantities of Egyptian seed received in the several ports are stated in the following table :—

Egyptian Cotton Seed shipped, 1910-1911

To	Tons
England	530,218
English Dependencies in the Mediterranean .	10
English Dependencies in the East	60
Germany	240,190
China and the East	349
United States of America	24
France	30,219
Greece	68
Holland	651
Italy	13
Wassana	2
Portugal	2
Turkey .	52
Total	801,858

The re-export of seed from the United Kingdom is quite insignificant ; it reached in 1906–1907 only 350 tons per annum.

The quantity of cotton seed oil exported from the United Kingdom is comparatively small, most of the cotton seed oil being consumed at home. The cotton seed oil exports are detailed in the following tables :—

Cotton Seed Oil exported from the United Kingdom

To	1910	1911	1912
	Tons	Tons	Tons.
Turkey .	1,500	1,040	1,162
United States of America	7,650	1,835	383
Germany	3,897	3,501	2,656
Holland .	6,290	4,537	4,160
Belgium .	3,624	3,981	3,917
Egypt .	213	25	367
Morocco .	155	477	677
French West Africa	1,303	1,552	1,296
Other foreign countries .	1,789	2,123	1,580
British possessions .	901	1,426	962
Total .	27,322	20,500	17,190

Crude and Refined Cotton Seed Oil Exports and Re-exports from the United Kingdom

CRUDE OIL

(All figures in Tons)

Country	Exports 1905	1906	1907	1908	1909	1910	1911	1912	Re-exports 1905	1906	1907
Norway	522										
Sweden		7	0								
Germany	4,210	84	3	7	78	43	40				
Holland	3,713	0	42	4,154	60	276	201				
Belgium	2,943	5	0								
France	426	7	6								
French West Africa											
Egypt											
Morocco											
Other foreign countries	774	16	7		56	60	91	276	59[1]	208[1]	134[1]
British possessions	149	40	12	61				264	92		
United States of America											
Total	**12,737**	**159**	**70**	**4222**	**194**	**379**	**332**	**540**	**151**	**208**	**134**

REFINED OIL

(All figures in Tons)

Country	Exports 1905	1906	1907	1908	1909	1910	1911	1912	Re-exports 1905	1906	1907	1908	1909	1910	1911
Norway									446	35	50	402	138	160	35
Sweden	728								253	140	4	106	110	279	102
Germany	1,618	4,911	3,682	2,580	2,072	3,897	3,504	2,656	700	900	233	428	477	108	11
Holland	533	5,294	7,237	7,611	4,905	6,290	4,537	4,160				40	406	3	4
Belgium	390	4,129	3,871	3,354	2,580	3,624	3,981	3,947				129			
France	702	7,049	9,781	4,685	3,169	2,179	1,869	2,692							
French West Africa	245	1,011	1,197	1,130	1,253	1,303	1,552	1,296							
Egypt	513	173	25	1,565	669	213	25	367							
Morocco		540	176	330	895	155	477	677							
Other foreign countries	456	2,232	2,224	1,706	1,920	1,789	2,123	1,580	133	116	377	61	180	119	85
British possessions	378	816	622	209	315	268	254	214	49	186	154	37	14	27	36
United States of America				33	686	7,650	1,835	383			901	153		281	38
Total	**5563**	**26,155**	**28,815**	**23,203**	**18,464**	**27,368**	**20,157**	**17,972**	**1581**	**1377**	**1719**	**1356**	**1325**	**977**	**311**

[1] Totals of all foreign countries

Physical and Chemical Characteristics of Cotton Seed Oil

At °C.	Specific Gravity		Solidifying Point		Saponification Value		Iodine Value	
		Observer	°C.	Observer.	Mgrs. KOH	Observer.	Per cent.	Observer.
15	0·923-0·925	De Negri and Fabris	3 – 4	Lewkowitsch	191-193	Lewkowitsch	100·9-116·9 [1]	Wiley
"	0·923-0·926 [5]	Shukoff	Below 12° "stearne" separates out from the oil.				106·9-110	De Negri and Fabris
"	0·9250	Lewkowitsch			191·8-193·8	De Negri and Fabris	106·5-108 [2]	Wallenstein and Finck
"	0·9203	Long			192-194·5 [5]	Shukoff	106·8 [3]	Lewkowitsch [1]
15·5	0·8725	Allen					105-110	Lewkowitsch
18	0·8672	Leone and Long					119·5-120·5 [4]	Shukoff
99/15·5							112-116 [5]	
100								

[1] American oil.   [2] Egyptian oil.   [3] Peruvian oil.   [4] Samarkand oil.   [5] Bombay oil.

Physical and Chemical Characteristics of Cotton Seed Oil—continued

Thermal Tests

Maumene Test		Heat of Bromination.		Specific Temperature Reaction.	
°C.	Observer	°C.	Observer		
75-76	Archbutt	19.4	Hehner and Mitchell	169-170	Thomson and Ballantyne
80-90	Wiley				
78	Tortelli[1]				

Refractive Index

At °C		Observer.
15	1.4748-1.4752	Stohmer
15.5	1.4733-1.4757	Tolman and Munson
25	1.4722	Harvey
60	1.4570	Thoerner

Oleo-refractometer

"Degrees" at 25° C.	Observer.
-20	Jean
+17 to +23	Pearmain

Butyro-refractometer.

°C	"Degrees"	Observer
15.5	72.3-75.6	Tolman and Munson
25	67.8	Beckurts and Seller
...	67.6-69.4	Mansfeld
40	53.4	White

[1] Tortelli = Thermometer

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Specific Gravity			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.	Iodine Value.		Refractive Index.	
Per cent.	Observer.	At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms KOH.	Observer.	Observer.	Per cent	Observer.	At 60° C.	Observer.
95.9	Lewkowitsch	15.5/4	0.92055-0.9219	Crampton	32	Allen	35.2	Allen	203.9	Valenta	275 Valenta	112-115	Thoerner	1.4460	Thoerner
		40/4	0.90497-0.90612	"	36	Dieterich	35-40	Thoerner	201.6	Thoerner		105-112	Lewkowitsch		
		50/4	0.89861-0.89972	"	32-35	Thoerner									
		100/4	0.86542-0.86574	"	Titer Test.							Iodine Value of the Liquid Fatty Acids.		Refractive Index of the Liquid Fatty Acids.	
		99/15.5	0.8467	Allen	32.2-32.7	Lewkowitsch	34-35	De Negri and Fahris				147.3-147.5	Wallenstein and Finck	Butyro-refracto-meter. "Degrees."	
					33.3-34.1	"	35-37	"				146.8-148.2	"		
					33.0-33.3	"	37-38	"				147.8	"	At 48° C.	
		100/100	0.8816	Arch-butt	34.4-35.2	"						149.4	"	53.7-51.4	Börner
					33.3-35.0	"						141.9-144.5	Lewkowitsch		
					35.6-37.6	"						148.9-151.7	Bomer, Tortelli and Ruggeri		
					28.1-28.5	"						147.3.7			

1 Part of the stearine taken out of the oil. 2 All the stearine left in the oil. 3 American oil. 4 Egyptian oil.
5 Peruvian oil. 6 Iodine value of oil 107.9-110.1 7 Iodine value of oil 105.3 8 "Winter oil."

The importations of cotton seed into France are stated in the following table :—

Year.						Tons.
1900	.	.	.	.	.	50,125
1901	.	.	.	.	.	46,959
1902	.	.	.	.	.	44,747
1903	.	.	.	.	.	30,158
1904	.	.	.	.	.	20,112
1905	.	.	.	.	.	35,502
1906	.	.	.	.	.	35,540
1907	.	.	.	.	.	38,548
1908	.	.	.	.	.	34,136
1909	.	.	.	.	.	32,340
1910	.	.	.	.	.	23,592
1911	.	.	.	.	.	30,550

The French imports and exports of cotton seed oil are summarised in the following table : —

Year	Imports	Exports.
	Metric Tons.	Metric Tons
1900	19,361	1834
1901	42,595	1880
1902	28,337	1425
1903	21,605	1196
1904	23,272	809
1905	42,072	1942
1906	37,129	2288
1907	34,060	2062
1908	46,749	2586
1909	23,959	2866
1910	3,900	1027
1911	9,262	653

In Germany cotton seed is expressed especially for the production of edible cotton seed oil for margarine, and this manufacture is confined to the north of Germany (Bremen, Northern Rhine). The cotton seed is imported from Egypt, from South America (Peru, Brazil), and latterly also from Bombay.

The growth of imports into Germany from 1908 to 1911 is shown in the following table :—

Cotton Seed imported into Germany

Year.						Tons
1908	.	.	.	.	.	52,528
1909	.	.	.	.	.	93,428
1910	.	.	.	.	.	106,232
1911	.	.	.	.	.	155,785
1912	.	.	.	.	.	214,097

In view of the rapidly increasing imports of cotton seed into Germany the following details may prove of interest :—

From	1911	1912
Egypt .	137,430	192,079
Brazil	3,508	2,479
United States of America	12,967	16,917

Germany imports cotton seed oil chiefly from this country and the United States of America. The imports from the latter country amounted in 1911 to 12,666 metric tons and in 1912 to 25,000 metric tons.

In Trieste cotton seed oil is being produced from Egyptian seed.

During the latter years cotton seed is also crushed in Turkestan : most of the seedlings of the cotton plant have been imported from Egypt and the United States of America (" upland " seed)   All the oil produced in Turkestan is consumed locally.

According to the latest available census of the United States Government there were in operation in 1911 the following numbers of cotton seed mills :—United States, 870 ; England, 25 , Egypt, 7 (consuming about 105,000 tons of seed out of a total production of 750,000 tons) , India, 1 (consuming about 10,000 tons a year out of a total production of 200,000 tons) ; Russia, 30 ; France, 5 , Germany, 6 , Mexico. 5 ; China, 10 [1] ; Peru, 15 ; Brazil, 27 ; other countries, 15.

Cotton seed is covered with woolly hairs, yielding the well-known cotton fibre.   In the case of Egyptian, Sea Island, and Jamaica cotton seed, this fibre is easily removable by means of suitable delinting machines, so that the seed can be crushed and pressed without previously removing the husk.   In the case of American upland seed, of Smyrna (Levant) seed, and especially of Bombay seed, the cotton fibre so tenaciously adheres to the husk that the usual delinting machines are unable to remove the whole of the hairs ; notably in the case of Bombay seed, a fine " down " adheres to the husk. Such seeds are decorticated in decorticating machines (" hullers ") before crushing. and the kernels (" meats ") are separated from the husks by means of another set of machines (" meats and hull separators "). Chemical processes for removing the " down " are resorted to less frequently. The principle underlying these chemical processes is the same that is made use of in carbonising " union " (wool and cotton) rags.[2] Another process [3] consists in treating with alkalis and molasses and then allowing to ferment ; the hulls are stated to separate readily from the kernels.

An examination made in the author's laboratory of various kinds of seeds yielded the following results :—

[1] A considerable amount of cotton seed oil is shipped from China to Australia, thus displacing oil previously shipped from this country.

[2] Cp. J. J. Green, English patent 12,539, 1902.

[3] Cp. United States patent 695,476.

Oil contained in Cotton Seeds (Lewkowitsch)

Kind of Seed	Kernels. Per cent	Husks. Per cent	Oil from		
			Whole Seed Per cent	Kernels. Per cent	Husks ("Hulls") Per cent
I. Maranhao .	58·8	41·2	21 54	36 0	0 9
II. ,, .	59·8	40·2	20 89	34 7	0·4
Coromandel			16		.
Egyptian (1899) .	60·0	40·0	21·98	37·41	
,, (1900) .	60 06	40·2	23 93	38·7	0·67
Mersyne . .	44·4	54·8	18 67	37 44	1 2
Bombay . .	51 0	49 0	20 56 [1]	39 28	1 08
American Upland			23 46		
Jamaica . .	60 0	40 0	23 6	39·3	0·37
Peru . .	...	..	35 2		..

It will be seen that the Levantine (Mersyne) seed yields the lowest percentage of oil. In this connection, it is noteworthy that seed of American and Egyptian origin grown at Bokhara contains only 17·5 per cent of oil.[2]

A distinction must be made between decorticated and undecorticated seeds. Undecorticated seeds are chiefly crushed in England, France, and Germany from Egyptian, Bombay, and also Smyrna seeds, whereas the vast majority of the American upland seed is crushed in the decorticated state. Also Bombay seed is decorticated in some establishments before crushing.

The kernels are permeated with cells containing deep brown colouring matter; hence the crude cotton seed oil running from the hydraulic presses has a ruby-red to almost black colour.

Cotton seed cake made from decorticated seed contains as a rule about 5 per cent of oil. The husks which remain in the cake are not detrimental to the cattle as long as the " non-fuzzy " variety of seed is used. The fuzzy-seeded varieties should not be employed in the undecorticated state for the production of cakes as the small fibres form " balls " in the stomach of the cattle. The " decorticated " cakes are usually ground to meal; in this form cotton meal is largely imported from the United States, especially by the Continent. Such cotton meal usually contains 10 per cent of oil. As this meal is as a rule light-coloured, attempts have been made (especially on the Continent) to " bleach " inferior meal by adding small quantities of borax, etc.

[1] This is somewhat high; the average percentage of Bombay seed is nearer 18 per cent. Cp. Wagner and Clement, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908, xvi. 147. (Seed from Madras, 17·41 per cent; Bombay, 17·66; Central Provinces, 19·65 per cent, United Provinces, 19·89 per cent.)

[2] For a method of " Rapid Determination of Oil in Cotton Seed Products " by C. H. Herty, F. B. Stem, and M. Orr, see *Journ. Ind. and. Eng. Chem.*, 1909, 76.

Thus " White " American meal is prepared. *Withers and Ray*[1] show that pyrophosphoric acid is not the cause of the toxic properties which have been observed in some cakes.

The depth of the colour of crude cotton oil depends in the first instance on the state of freshness of the seed. The American seed, which is to a large extent crushed immediately after having been harvested, yields a crude oil of much paler colour than that of crude oil obtained in England, France, and Germany from Egyptian and other seed. The palest Egyptian or Indian crude oil is obtained from freshly arrived seed. When the seed is stored for several months it undergoes some deterioration (" heating," which may also occur during the voyage) ; hence the crude oil obtained from Egyptian seed in July and August has the darkest colour.

In the American trade three grades of crude cotton seed oil are recognised, viz. " prime," " choice," and " off " qualities. The following are the recognised definitions of these three grades :—

" *Prime crude* cotton seed oil must be made from sound decorticated seed, must be free from water and foots, and must be sweet in flavour and odour. It should produce prime summer yellow oil when refined with caustic soda, with a loss in weight not exceeding 9 per cent. Should the loss in refining be greater than 9 per cent, but the oil obtained be still of prime summer yellow grade (and it cannot be rejected by the buyer), the price must be reduced by a corresponding amount."

" *Choice crude* oil must be manufactured from sound decorticated seed, must be free from water and foots, sweet in flavour and odour, and should produce by proper methods of refining choice summer yellow oil, with no greater loss in weight than 6 per cent for Texas oil and 7 per cent from oil of other seeds. The percentage of free fatty acids should not exceed 1 per cent (as oleic acid).

" Qualities which correspond to neither of the grades mentioned are termed ' *off* ' oil, and are sold by sample."

A characteristic test of crude oil is the following :

On saponifying crude oil with caustic potash, the upper layers which are exposed to the air become blue and afterwards violet a very characteristic reaction of crude cotton seed oil. If alkali be used in insufficient quantity to produce complete saponification, the colouring matter is carried down together with the soap formed, so that the supernatant oil is but slightly yellowish.

On this reaction is based the technical method of refining cotton seed oil. The oil is warmed (to 120° F.) and then intimately intermixed with dilute caustic soda solution. The proportion of caustic soda required depends on the quality of the oil ; only so much caustic soda should be added as is necessary to combine with the colouring matter and the free fatty acids in the oil. Sufficient caustic soda has been added when a sample examined on a glass plate appears " broken." Caustic soda when applied in excess causes saponification, and in that case the whole mass is apt to form a homogeneous mixture, which very frequently refuses to separate into two layers. If a judicious amount

[1] *Journ. Biol. Chem.*, 1913 (14), 53.

of caustic soda has been added, which is generally ascertained in the works laboratory by a small scale test, the mixture will readily separate, on standing, into two layers. The upper layer consists of decolourised oil; the lower one forms a black to light brown heavy liquid ("mucilage"), this being a solution of dark brown colouring matter [1] in the soap resulting from the union of free fatty acids and caustic soda.

The mucilage also contains some neutral oil, which has been mechanically carried down or has been emulsified by the soap solution. The mucilage from fresh oil, especially from American crude oil, is of comparatively light colour. A large quantity of mucilage, especially in America, is therefore converted into soap, after removing the bulk of the colouring matter in the soap pan by "cutting" the soap with alkali. The soap so obtained is sold at a low price as "foots soap" (Vol. III. Chap. XVI.). Dark-coloured mucilage is treated with mineral acid, the separated fatty mass is distilled, and the distillate worked up for oleine and stearine (Vol. III. Chap. XVI.).[2]

The supernatant oil (the upper layer) is then drawn off and washed with warm water. Since alkalies are used in refining cotton seed oil, the fact that commercial cotton seed oil is practically free from fatty acids is readily explained.

The loss in refining depends on the freshness of the oil and the care exercised by the manufacturer. The permissible losses in American crude oil have incidentally been given above. In the United Kingdom the refiners use more care than the American oil millers, and the losses are therefore considerably smaller. The smallest losses are made in November, December, January, February, increasing in the months following owing to old seed being employed.

If the oil be intended for edible purposes it must not be bleached with chemicals, whereas for commercial purposes—"soap oil"—the oil is bleached with bleaching powder and mineral acid, and then washed with water until the mineral acid has been removed completely.

In the American trade three kinds of refined oils are discriminated, viz. "Prime summer yellow," "Choice summer yellow," and "Off summer yellow" oils. *Prime summer yellow* oil is required to be clear, free from water and foots, sweet in flavour and odour, and of no deeper colour than 35 parts yellow and 7·1 parts red in *Lovibond's* tintometer. *Choice summer yellow* must be clear, free from moisture, and sweet in flavour and odour. *Off summer yellow* must be free from water and foots, and may be of lower quality as regards taste and colour. The refined oil is graded in the United States according to colour. The Interstate Cotton Seed Crushers' Association has adopted as the standard for grading refined oil *Lovibond's* tintometer. Thus prime summer oil

[1] Experiments have been made repeatedly to recover the brown colouring matter, which has been termed "Gossypol", all the patented processes having for their object the commercial preparation of the colouring matter have so far ended in failure Methods of separating the resinous substances from the fatty matter have been patented by Stuepel, German patent 219,716, and Loeschigk, German patent 220,582.

[2] English patent 22,231, 1900 (British Oil and Cake Mills and A. G. Wass), claims the manufacture of printing ink from mucilage. Cp. also J. C. Chisholm, United States patent 1,056,261.

must not have a deeper colour at about 70° F. than the combination
of 35 yellow units and 7·1 red units of *Lovibond's* tintometer shows.
The oil intended for edible purposes is bleached with fuller's earth (see
Chap. XIII.).

Cotton seed oil is suitable for edible purposes, but popular prejudice
has largely militated against the edible quality being sold under its true
name. Hence, the oil has appeared in the market under the disguise
of such names as " table oil," " salad oil," " sweet nut oil," " butter oil,"
etc. Enormous quantities of the " butter oil " quality are used in the
manufacture of margarine and compound lards. The commercial
brands " summer oil " and " winter oil " differ in that the winter oil
has the bulk of the " stearine " removed, so that the oil should remain
fluid, even during the winter. Such winter oil or " demargarinated " oil
is characterised by a low titer test. Thus the titer test of a sample of
demargarinated oil manufactured by the author on a commercial scale
was 28·1°-28·5° C.

Two grades of winter oils are recognised at the New York Produce
Exchange : " prime winter white " cotton seed oil, and " prime winter
yellow " cotton seed oil. Prime winter white cotton seed oil must be
perfectly clear, straw-white to white in colour, sweet in flavour and dry,
and must remain clear, at a temperature of 32° F., for five hours. Prime
winter yellow cotton seed oil must be transparent, free from water and
foots, sweet in flavour and odour, straw coloured (not reddish), and
must remain clear, at a temperature of 32° F., for five hours. The cold
test relied upon must be carried out as follows : A 4-oz. sample bottle
is filled with the oil, a thermometer inserted through the cork of the
bottle, and closed tight. The oil is then warmed slowly to 80° F. and
allowed to remain at that temperature for fifteen minutes. It is then
put into a box surrounded by ice and allowed to stand in the box for
five hours. After this time it must still be clear, brilliant, and free from
" stearine."

As a by-product of winter oil there is obtained "cotton seed stearine" [1]
(French—*Margarine de coton, Margarine régétale.* German *Baum-
wollstearin, Vegetabilisches Margarin.* Italian—*Margarina di cotone*),
a light-yellow fat of buttery consistence. This cotton seed stearine is
manufactured on a large scale, especially in the United States, in the
process of producing " winter oil," by cooling cotton seed oil, draining
off or filtering off the solid deposit, and pressing the latter.

Since cotton seed stearine forms an article of commerce, and is
largely used in the manufacture of lard and butter substitutes, it may
be of use to record the physical and chemical characteristics (see tables,
pp. 198, 199).

It should be noted that, according to the pressure employed in
the manufacture, cotton seed stearine contains a larger or smaller
proportion of liquid glycerides ; hence, the great divergence of the
solidifying and melting points recorded in the table is easily explained.

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[1] With the above described cotton seed stearine there must not be confounded the
cotton seed "stearine" obtained by distilling the fatty acids obtained from cotton seed
oil "mucilage" (cp. Vol. III. Chap. XVI.).

The behaviour of cotton seed stearine in the colour tests is the same as that of cotton seed oil itself. The same holds good of the chemical composition, with this limitation, however, that the proportion of solid fatty acids is larger than in cotton seed oil. Thus *Hehner and Mitchell* found in a sample of cotton seed stearine 3·3 per cent of stearic acid.

Recent observations by the author have shown that it is doubtful whether stearic acid does occur in cotton seed oil, inasmuch as it was found that 5 or more per cent of stearic acid dissolved in the mixed cotton seed fatty acids could not be thus detected. According to *Victor J. Meyer* [1] the " stearic " acid found by this method is most likely arachidic acid, or a mixture of palmitic and arachidic acids, since *Meyer* was unable to detect stearic acid in the methylesters of the cotton seed oil fatty acids (see Vol. I. Chap. XII. and following page).

According to the amount of " stearine " left in the oil, the proportion of glycerides of solid fatty acids in cotton seed oil vary ; therefore such widely different percentages of solid fatty acids as are stated by *Twitchell, Farnsteiner, Tolman and Munson*, viz. from 22·3 to 32·6 per cent, are readily explained. *Boley* (in the author's laboratory) found in a number of American and Egyptian cotton seed oils proportions of solid fatty acids varying from 20·92 to 21·18 per cent.

The solid fatty acids consist chiefly of palmitic acid ; small quantities of arachidic acid appear to be present.

No ether-insoluble bromides having been obtained from cotton seed oil, linolenic acid may be considered to be absent. The liquid fatty acids seem to consist of oleic and linolic acids only. *Hazura* [2] stated that the liquid fatty acids consist approximately of 60 per cent of linolic and 40 per cent of oleic acid. The proportion of linolic acid in the mixed fatty acids as calculated from the isolated linolic tetrabromide melting at 113-114° C. was 18·45 per cent (*Farnsteiner*) and 21 per cent (*Lewkowitsch*). From the liquid fatty acids *Farnsteiner* obtained linolic tetrabromide corresponding to 23·9 per cent linolic acid. From the percentage composition of 23·45 per cent linolic acid and 76·55 per cent oleic acid would follow the calculated iodine value of the liquid fatty acids = 111·5. Since direct experiments (cp. table, p. 190) lead to the iodine value of the liquid fatty acids of approximately 150, the amount of linolic tetrabromide found would appear to be much below the truth. For further experiments made to explain the discrepancy cp. Vol. I. Chap. VIII. p. 576.

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[1] *Chem. Zeit.*, 1907. 791.   [2] *Zeitschr. f. angew. Chem.*, 1888, 315.

Physical and Chemical Characteristics of Cotton Seed Stearine

Specific Gravity			Solidifying Point		Melting Point		Saponification Value		Iodine Value		Maumené Test	
At °C		Observer.	°C.	Observer.	°C	Observer.	Mgrms. KOH	Observer.	Per cent.	Observer.	°C.	Observer.
99 (water 15.5=1)	0·8684	Allen	31·32.5	Allen	40	Allen	...	...	89·8	Allen	48	Hart
15	0·91884	Crampton	...	...	...	...	194·6	Hart	93·6	Hart		
							194·8- 195·1	Lewko- witsch				
40	0·90313	,,	...	...	39	Mayer	...	...	88·7	De Negri and Fabris		
50	0·89671	Hart			30·31	Hart						
100	0·867	,,			26·29	De Negri and Fabris			92·7	Lewko- witsch		
,,	0·86463	Crampton	16·22	De Negri and Fabris			...	...	92·8	Schweitzer and Lungwitz		
									99·2-			
									103·8			

Titer Test Method.

16-16·05	Lewkowitsch
22	,,

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Solidifying Point Titer Test		Melting Point		Iodine Value	
Per cent.	Observer.	°C.	Observer	°C.	Observer.	Per cent	Observer
95·5	Muter	34 9-35 1	Lewko-witsch	27-30	De Negri and Fabris	94 3	De Negri and Fabris
96 3	Hart	40·8[1]	,,				

The fractional distillation of the methylesters· of cotton seed oil fatty acids boiling above 200° C. at 18 mm. pressure gave the results detailed in the following table (*Victor J. Meyer*) : —

Fraction	Boiling Point	Pressure	Quantity obtained from 535 Grams of Oil	Iodine Value
		mm	Grams	
I.	up to 201 5	16	8	77·13
II.	201 5-204	16	9	101 19
III.	204 -207 5°	16	20	123 51
IV.	207·5-210·5°	16	83	130 87
V.	210 5-214·5°	16	11	123 83
VI.	above 214·5°	16	2	107·23

The iodine values enumerated in the last column confirm the above statement that oleic acid and linolic acid only are present amongst the unsaturated fatty acids of cotton seed oil, to the practical exclusion of linolenic acid ; for the methylesters of oleic acid and linolic acids have the theoretical iodine values 85·82 and 172·78 respectively.

On oxidising the unsaturated fatty acids of cotton seed oil two tetrahydroxystearic acids are obtained, melting at 155·5°-156·5° C. and at 173° C. respectively (*Hazura, Hartley* [2]). This fact lends support to the view that two linolic acids exist.

The acetyl values of various samples of cotton seed oil were found by the author [3] to vary from 7·6 to 18, according to the state of freshness of the oil. There was, however, no strict parallelism noticeable between the amount of total volatile acids and the acetyl value.

Cotton seed oil eminently typifies a semi-drying oil. In the *Livache* test it absorbs 5·9 per cent of oxygen in twenty-four hours. By blowing air through cotton seed oil at a temperature of about 90°-100° C. oxygen is absorbed, with the formation of a small amount only of oxidised acids,

[1] The author is informed that some cotton seed stearines produced in the United States of America have still higher titer tests.

[2] *Journ. of Phys.*, 1909 (38), 366.   [3] Lewkowitsch, *Analyst*, 1899, 319.

the acetyl value rising at the same time considerably. This is shown in the following table, reproducing some experiments made by the author.[1] (Cp, also " Blown Oils," Chap. XV.)

	Specific Gravity at 15·5° C.	Total Volatile Acids per Gram in terms of Milligrams KOH.	Oxidised Acids. Per cent.	True Acetyl Value.
Cotton seed oil	0·9250	0·1	...	7·6
Cotton seed oil, blown two hours at 120° C	0·9262	2·88	0 51	11 32
Cotton seed oil, blown four hours at 120° C	0 9291	2·44	0·87	20·46
Cotton seed oil, blown six hours at 120 C.	0 9350	4 60	0·94	25·4
Cotton seed oil, blown ten hours at 120 C	0 9346	4 16	1·28	30·81

In the following table are contained the numbers obtained by *Procter and Holmes*.[2]

Blown	Specific Gravity.	Refractive Index	Iodine Value
Hours			
0 [3]	0 920	1 4745	106 0
3	0 926	1·4745	105·0
6	0·926	1 4746	98·0
9	0 926	1 4750	97 0
12	0 927	1·4751	97 0
15	0 929	1·4752	96 0
18	0 929	1 4757	91 0
21	0 931	1 4758	91·0
24	0 936	1 4759	91 0

The mixed fatty acids do not absorb oxygen as rapidly as does the oil itself. Thus in the *Livache* test only 0·8 per cent were absorbed, as against 5·9 per cent in the case of the oil from which the fatty acids had been derived.

In the claudin test a mass is obtained of pasty and buttery consistence.

Cotton seed oil is readily reduced by hydrogen in the presence of a catalyst to a hard fat, the iodine value of which can be brought to almost *zero*. (Cp. Vol. III. Chap. XV. " Hydrogenised Fats," " Hardened Fats.") Such reduced cotton seed oil gives neither the *Becchi* nor the *Halphen* colour reaction (see below).

Cotton seed oil is readily recognised by the high melting and solidifying points of its fatty acids. This characteristic difference from similar

oils renders the identification of cotton seed oil a comparatively easy task. This also greatly facilitates the detection of it in other oils and fats. Thus pure maize oil can be easily distinguished from cotton seed oil by the titer test of its fatty acids. The iodine value of natural cotton seed oil is also important for purposes of identification, especially so the iodine value of its liquid fatty acids, although the iodine numbers are less characteristic than the solidifying and melting points.

The unsaponifiable matter in cotton seed oil varies from 0·73 to 1·64 per cent, and consists to a great extent of sitosterol, in admixture with non-crystallisable colouring matters. Hence, the characteristic "phytosterol crystals" can but rarely be isolated in a rapid manner from the unsaponifiable matter. According to *Bomer and Winter* [1] the crude sitosterol requires to be recrystallised seven or eight times, before the pure substance, melting from 136°-137° C., can be obtained. In the phytosteryl acetate test the unsaponifiable matter yields crystals melting from 123·5°-124° C.

Siegfeld [2] obtained from cotton seed oil 0·972 per cent of crude "phytosterol." On recrystallisation from hot alcohol, a resinous dark yellow substance was found adhering to the glass. This substance was completely insoluble in alcohol. From the first mother liquor crystals of indistinct form separated ; these were purified separately. After the first crystallisation, they showed well-formed plates, obtruncated at both ends. The melting point after the fifth crystallisation was 92·7°-93·7° C. This substance could not be acetylated. After the usual treatment with acetic anhydride, on recrystallising, laminæ of the same form were obtained ; the melting point of these was, after the third crystallisation, 92·6°-93·6° C.

The first crystallisation of the unsaponifiable substance showed no definite form, and was strongly contaminated with oily substances. The second crystallisation yielded long, hard, brittle needles melting after the ninth crystallisation at 121·8°-122·2° C. After treatment with acetic anhydride, the substance yielded exactly the same crystals, melting after the second crystallisation at 121·8°-122·8° C. It was only from the mother liquors of the substance that sitosterol could be obtained in its characteristic crystals. The melting point of the sitosterol after the fifth crystallisation was 138·8°-139·8° C. The melting point of the acetate after the sixth crystallisation was 131·5°-132·5° C. It would therefore appear that *Bomer's* acetate of the melting point 123·5°-124° C. was a mixture of *Siegfeld's* substance, melting at 121·8°-122·8° C., with a certain amount of the true acetate melting at 131·5°-132·5° C.

Heiduschka and Gloth [3] were unable to detect stigmasterol in the unsaponifiable matter of cotton seed oil. They obtained from the unsaponifiable matter a dibromo-phytosterol melting at 127° C.

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1901, 872.
[2] *Ibid.*, 1904, 581. Cp also Kœnig and Schindelmeiser (*Ibid.*, 1908, xv. 653), who give as melting point of frequently recrystallised "phytosterol" 137 and 138 C. and the melting points of third, fourth, and fifth crop of its acetate as 123·6°, 124·8°, and 125·8° C. respectively.
[3] *Pharm. Zentr.*, 1908 (49), 863.

Wagner and Clement [1] found in the unsaponifiable matter from " soap stock " (Vol. III. Chap. XVI.) in which the unsaponifiable matter accumulates, two alcohols, one melting at 139° C. and the other at 130°-131° C. The former gave a dibromide, the acetate of which melted at 122°-123° C. and decomposed at 145° with evolution of hydrobromic acid. The second alcohol (melting at 130°-131° C.) gave an acetate melting at 120° C., the dibromide of which melted at 114°-115° C. and decomposed with evolution of hydrobromic acid at 148° C. *Wagner and Clement* concluded that these two alcohols are different. *H. Matthes and W. Heintz*, [2] however, found in a thorough study of the unsaponifiable matter of cotton seed oil (by resolving it into a solid and a liquid portion) that the solid portion consists of a phytosterol (sitosterol) melting at 139° C. (see Vol. I. p. 276) and a substance melting at 81°-82° C. representing an amorphous yellowish mass, and a dextro-rotary oxygen-containing unsaturated substance melting at 172°. The dextro-rotation excludes the presence of stigmasterol (thus confirming *Heiduschka and Gloth's* observation), to the presence of which the high melting point would naturally direct attention. The liquid portion was resolved by fractional distillation *in vacuo* into 5 fractions, boiling from 98° C. up to 300° C. (the 4 last fractions of which absorbed respectively 91·1, 123, 102, 112 per cent of iodine). The unsaponifiable matter did not give the *Becchi* reaction.

Cotton seed oil, being one of the cheapest fatty oils, is not liable to adulteration. Still, at times when linseed oil, maize oil, and soya bean oil are much cheaper than cotton seed oil, admixture with these oils may occur. Linseed oil is detected by the higher iodine value of the sample, and notably by the bromide test. The detection of soya bean oil and maize oil is a more difficult problem, which requires systematic application of the methods detailed in Vol. I. Chap. VIII. (cp. also Chap. XII.).

Edible cotton seed oil is employed in immense quantities as a table oil and in the manufacture of margarine, and besides these legitimate uses, for the adulteration of olive oil, lard, and other edible oils and fats. The detection of cotton seed oil in these oils and fats thus becomes one of the most important objects of fat analysis. It is therefore not surprising that the literature on this subject is very voluminous. A number of colour tests have been recommended for the identification of cotton seed oil and its detection in other oils. The opinions of various observers as to the value of one or other of these colour tests differ greatly. This divergence of statements is in no small degree due to the difference of age and source of the specimens examined. With regard to the latter, it should be noted that American oils differ somewhat from Egyptian oils in their behaviour to the reagents used for the colour reaction.

The author has examined the various colour reactions proposed, and found most of the older tests useless. Hence they are omitted here. [3]

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909 (xvii.), 267.
[2] *Archiv d. Pharm.*, 1909 (247), 161.
[3] Cp. second edition of this work, p. 384.

The few colour tests that will be discussed are certainly of assistance to the analyst, but it should be distinctly understood that colour reactions taken by themselves should not be relied upon as giving a decisive answer. At best they can only be used as a preliminary test, or as a confirmatory test.

The best colour test for the identification of cotton seed oil, and for the detection of it in other oils and fats, provided the cotton seed oil has not been heated, is the **Halphen colour reaction**. This test is carried out in the following manner :—1 to 3 c.c. of the oil is dissolved in an equal volume of amyl alcohol ; to this is added 1 to 3 c.c. of carbon bisulphide holding in solution 1 per cent of sulphur (flowers). The test-tube containing the mixture is then immersed in boiling water, and kept therein for some time. The carbon bisulphide evaporates off, and cotton seed oil gives in the course of five to fifteen minutes a deep red colouration. This colour reaction is most characteristic, and it is possible to detect thereby 5 per cent, and even less, of cotton seed oil in admixture with other oils and fats, e.g. olive oil or lard. In cases where the proportion of cotton seed oil is small, the test-tube must be kept in the water-bath for twenty to thirty minutes, or preferably in a salt-bath at 105° C.[1] Mixtures of olive and arachis oils containing 1 per cent of cotton seed oil gave in the author's laboratory distinct colourations after twenty-five to thirty minutes.

The ease with which this test can be carried out, and its apparent reliability, have led to an over-estimation of this very useful and important reaction ; so much so that grave errors may be committed by those who assign to this test an exclusive, or even a paramount, importance. It is altogether unjustifiable to look upon this test, as has been done, as permitting of quantitative interpretation.

Up till recently it was entirely unknown what substance produces the colour reaction in the *Halphen* test, and all conjectures as to its aldehydic nature or otherwise [2] rest on unfounded assumptions. *E. Gastaldi* showed that purest amyl alcohol gives a very faint reaction, whence he concludes that the colour reaction is produced by impurities contained in commercial amyl alcohol. Indeed *Gastaldi* showed [3] that amyl alcohol may be replaced in the *Halphen* test by a drop of pyridine, aniline, chinoline, or a few drops of concentrated ammonia, or a concentrated solution of caustic soda or caustic potash. The chromogenetic substance appears to be present in very small quantities only, and is also retained by cotton seed cake ; it has the property of passing into the body fat of pigs and cattle fed with cotton cake.

[1] In order to perform the reaction at a still higher temperature Stemmann (*Schweiz. Wochenschr. f. Chem. und Pharm.*, 1901 (39), 560) proposed (unnecessarily) to add amylalcohol to the Halphen reagent.

[2] Cp. Soltsien, *Zeitschr. f. offentl. Chemie*, 1899, 306 ; Charabot and Marsh, *Bull. Soc. Chim.*, 1899, 552 ; Raikow, *Chem. Zeit.*, 1899, 760, 892 ; 1900, 562, 583 ; 1902, 10 ; Gill and Denison, *Journ. Amer. Chem. Soc.*, 1902, 397 ; Kaigashew, *Pharm. Journ.*, 1905 (14), 1229 ; Rupp, *Zeits. f. Unters. d. Nahrys- u. Genussm.*, 1907, xiii. 74 ; Petkow *Zeitschr. f. offentl. Chemie*, 1907, 21. See also footnote 1, p. 207. L. Garnier, *Ann. Chem. analyt.*, 1909 (14), 209 ; L. Ronnet, *Journ. Pharm. Chim.*, 1909 (29), 379 ; R. Marcille, *Annales des Falsif.*, 1910, 235.

[3] *Annali del Laborat. Chim. Centr. delle Gabelle*, vol. vi., 1912, 601.

Hence the *Halphen* colour reaction can be obtained with lards, etc., which are absolutely free from admixed cotton seed oil.

It should further be noted that failure to obtain the colour in the *Halphen* test does not prove the absence of cotton seed oil. For the chromogenetic substance is destroyed by heating cotton seed oil to 250° C., or even by keeping it at 200° C. for some prolonged time,[1] or by blowing cotton seed oil with air (*Lewkowitsch*), or treating with fuming hydrochloric acid,[2] sulphurous acid,[3] and chlorine. Cotton seed oil so treated no longer gives the *Halphen* colour reaction. Blown cotton seed oil (Vol. III. " Blown Oils ") and even old rancid oil cannot therefore be identified by the *Halphen* test.

Hence a negative *Halphen* test in a suspected sample is no conclusive proof of the absence of cotton seed oil. Cotton seed oil fatty acids do not show the colour test as distinctly as the oil itself. Frequently the mixed fatty acids obtained by saponifying cotton seed oil give a very faint red colouration only, or even none at all, most of the colouring matter having either been destroyed or washed away in the process of isolating the mixed acids (*Lewkowitsch*).

Finally *Halphen's* test can no longer be considered as exclusively due to cotton seed oil. Kapok oil and baobab oil[4] give the same colour reaction, and the last-named oil with even greater intensity than cotton seed oil (*Millian*).

In case a negative *Halphen* test be obtained on examining a sample, and the presence of heated cotton seed oil be suspected, confirmation may in some cases be obtained by the nitric acid test. This test is best carried out with nitric acid of 1·375 specific gravity, as the author has ascertained by a number of experiments. A few c.c. of the sample are shaken energetically with an equal measure of nitric acid of the specified gravity, and the sample allowed to stand for some time, up to twenty-four hours. Cotton seed oil gives a coffee-brown colouration which is characteristic of this oil to such an extent that admixtures of 10 to 20 per cent of cotton seed oil to olive oil can be detected in certain cases.[5] But even here great circumspection is necessary, as the coffee-brown colouration given by some specimens of cotton seed oil is not characteristic of all cotton seed oils. Thus the author has met with many American cotton seed oils that gave the nitric acid test so faintly that olive oils mixed with 10 per cent of this cotton seed oil showed no coffee-brown colouration. Important is the observation made by the author, viz. that a specimen of heated cotton seed oil which no longer gives the *Halphen* test still gives the brown colouration with nitric acid, and that also the fatty acids from this specimen of heated cotton seed

[1] Oilar (*Amer. Chem. Journ.* 24, 355) states that heating for one hour to 140°-150° C. in a steel pan suffices to nullify the Halphen colour test.

[2] Kuhn and Bengen, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1906 (xii.), 149

[3] Fischer and Peyau, *ibid.*, 1905 (ix.), 81

[4] *Compt. rend.*, 1904 (139), 807.

[5] Soltsien (*Chem. Revue*, 1908, 29) raises an objection against this test on the ground that olive and hazelnut oils heated to 250° C. also give a brown colouration. This "objection" is quite unintelligible, for no manufacturer would heat edible olive and hazelnut oils in order to substitute them for cotton seed oil.

oil showed the colouration distinctly. This proves incidentally that there are at least two chromogenetic substances present in cotton seed oil.

The Silver Nitrate Test.—This test was first proposed by *Becchi*, and although it has been persistently condemned by a number of observers, it is still being employed by many chemists, especially in France and Italy ; hence a discussion of this test must find a place here. Several years ago the Italian government appointed a special committee to inquire into the value of this test, and according to the report given by *Del Torre*, the following two reagents are required . —

<div align="center">

REAGENT I

</div>

Silver nitrate	.	1 00 grm.
Alcohol, 98 per cent (by volume)		200 0 c c.
Ether	.	40 0 c c.
Nitric acid	.	0 1 grm

<div align="center">

REAGENT II.

</div>

Amyl alcohol	100 c.c.
Colza oil .	15 c.c.

The test is carried out as follows   10 c c. of the oil under examination are mixed in a test tube with 1 c.c. of reagent I., and then shaken with 10 c c. of reagent II. The mixture is next divided into two equal portions, one of which is put aside for comparison later on, whereas the other is immersed in boiling water for a quarter of an hour. The heated sample is then removed from the water-bath and its colour compared with that of the first portion. Presence of cotton seed oil is indicated by the reddish-brown colouration of the heated portion. *De Negri and Fabris* lay stress on the necessity of using the purest alcohol. The colza oil used should be " cold-drawn " oil, and only slightly coloured ; it should be filtered in a hot water oven before preparing the reagent. To guard against possible errors arising from the impurity of the reagents a blank test should be instituted side by side with the actual test.

Peruzzi, Rudolfi, Roster, and Wiley tested *Becchi's* method in the case of over 200 samples of cotton seed oil, and found it thoroughly reliable, no other oil giving them the brown colouration. *Holde,*[1] on the contrary, considers the test as absolutely valueless , but the experiments of *De Negri and Fabris*, as also tests made repeatedly by the author *(see below), prove that *Holde's* statements are too sweeping, having most likely been deduced from observations on the particular sample he examined.

The *Becchi* test is too capricious to be recommended. Moreover, it is difficult to understand why colza oil is introduced ; frequently even serious errors are thereby caused.

The statements contained in the literature on *Becchi's* test are of a most conflicting nature.

[1] *Journ. Soc. Chem. Ind.*, 1892, 637.

Benedikt found that some samples of cotton seed oil do not reduce *Becchi's* reagent either with or without the addition of colza oil. Since *Becchi* himself states that old samples of cotton seed oil only reduce the silver nitrate when colza oil has been added, the value of all the modifications proposed becomes doubtful.[1] The author examined mixtures of Egyptian cotton seed oil with olive oil, and finds that an admixture of 10 per cent of cotton seed oil can be detected with certainty, whereas in the case of 5 per cent the reaction becomes indistinct. The silver nitrate test can, therefore, only be relied upon as decidedly indicating the presence of cotton seed oil if a positive reaction has been obtained. Absence of colouration, however, does not prove absence of cotton seed oil. Since even pure lard (see " Lard "), as *Wesson* stated, gives a slight colouration with silver nitrate, and furthermore, as olive oils are often met with which give the *Becchi* reaction to a very marked extent (*Milliau*), even the appearance of a brown colour should not be considered as absolute proof of adulteration with cotton seed oil.

Milliau modifies *Becchi's* test by adding the silver solution to the **mixed fatty acids** instead of to the neutral oil.

Milliau[2] proceeds as follows :—5 c.c. of the fatty acids of the sample are dissolved in 15 c.c. of 95 per cent alcohol, and heated in a water-bath to 90° C. Two c.c. of a 30 per cent solution of silver nitrate are then added, and the mixture is again heated until about one-third of the alcohol has evaporated. If the sample be cotton seed oil, or contain cotton seed oil, the silver nitrate is reduced to metallic silver, producing a black or brown colour in the liquid, or giving particles of reduced silver. Even 1 per cent of cotton seed oil, as *Milliau* states, can thus be detected. *Wiley*[3] considers this test a very useful one, whereas *Hehner*[4] sees no advantage in this modification of *Becchi's* test, an opinion in which the writer fully concurs. In many samples, where cotton seed oil was present and was indicated by *Becchi's* test, I could not obtain the reaction.

This fact is explained by an observation made by a French Committee, consisting of *Muntz, Durand, and Milliau*, viz. that by washing the free fatty acids repeatedly, the substances (supposed to be of an aldehydic nature) which produce the colour reactions are washed away. They therefore recommended not to melt the fatty acids, so as to retain the chromogenetic substance in the mixed fatty acids. *Milliau* proceeds in the following manner :—

15 c.c. of the oil are saponified in a 250 c.c. porcelain dish with alcoholic potash, and the soap is dissolved in 150 c.c. of distilled water. The alcohol is evaporated off by boiling, and the fatty acids are liberated by adding a slight excess of dilute sulphuric acid. The solution must not be boiled in order to melt the separated fatty acids, as otherwise the aldehydic substances may pass into the aqueous solution. The emulsified acids are taken off and washed in a wide test tube three times

[1] Wilson also (*Chem. News*, 59, 99) states that cotton seed oil, after keeping for some time, loses its power of reducing silver nitrate.
[2] *Compt. rend.*, 1888 (106), 550 ; *Journ. Soc. Chem. Ind.*, 1893, 716.
[3] *Lard and Lard Adulterations*. Washington, 1889, 467.
[4] *Analyst*, 13, 165.

each with 10 c.c. of cold distilled water. Finally, the fatty acids are dissolved in 15 c.c. of 92 per cent alcohol, and 2 c.c. of a 3 per cent silver nitrate solution are added. The test tube is placed, protected from light, in a water-bath and heated to 90° C. until one-third of the alcohol has evaporated off. Ten c.c. of hot distilled water are then added, and the heating continued for a few minutes. In the presence of cotton oil, the fatty acids which float on the top are black, owing to the separation of metallic silver. If the proportion of cotton seed oil exceeds 15 per cent, the aqueous solution is also coloured.

Jean's proposal, to decompose the soap solution obtained on saponifying the oil under petroleum ether, is preferable. The fatty acids, as they are librated, pass into the petroleum ether, carrying with them the chromogenetic substance ; when the petroleum ether solution is subsequently washed, the chromogenetic substance is not removed.

The reduction of silver nitrate is stated to be effected by a substance of an aldehydic nature, the properties of which have not yet been investigated.[1] It should be noted that the silver reducing substance is destroyed or oxidised by heating cotton seed oil or its fatty acids to 240° C. (*Wesson*), or even by keeping the sample or the free acids for some time. Therefore, cotton seed oil heated to 240° C. cannot be identified or recognised in other fats by *Becchi's* or *Milliau's* tests.

Tortelli and Ruggeri [2] state that the *Milliau* test becomes more delicate on examining the liquid fatty acids in the following manner :— 5 grms. of the liquid fatty acids of the suspected sample are dissolved in 10 c.c. of alcohol, and 1 c.c. of a 5 per cent silver nitrate solution is added ; the sample is then heated on a water-bath to 70°-80° C. Cotton seed oil reduces the silver immediately, whereas olive oil and other oils remain clear for some time. Even cotton seed oil—which had been heated to 250° C. for ten and twenty minutes respectively—could be recognised when present in as low a proportion as 10 per cent in olive oil, on allowing the liquid fatty acids of the mixed oil to stand in the hot water-bath for several hours.

From the foregoing remarks it is obvious that the colour reactions can only be used as subsidiary, or at best as confirmatory tests, and that the *Halphen* test should be supplemented in the case of heated oils by the nitric acid test or by the modified *Milliau's* test suggested by *Tortelli and Ruggeri.* The main attention of the analyst should be directed to the indications furnished by the iodine value of the oil (or its mixed fatty acids), the iodine value of the liquid fatty acids, and the solidifying and melting points of the mixed fatty acids. In case an animal oil or fat is suspected of being adulterated with cotton

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[1] Dupont (*Bull. Soc. Chim.*, 1895 [3], 696 , *Bull. Chem.*, 1895, 811), having obtained on passing a current of steam through cotton seed oil a volatile substance yielding sulphuric acid on oxidation, ascribes the Becchi reaction to the formation of silver sulphide. But as the remaining oil still gave the Becchi test, proof for Dupont's opinion is wanting. Raikow (*Chem. Zeit.*, 1899, 769) did not obtain the volatile sulphurised substance, but its occurrence is confirmed by Fischer and Peyan (*Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905 (ix.), 81). Matthes and Heintz state most distinctly that the unsaponifiable matter in cotton seed oil is *free* from sulphur.

[2] *Annali del Laborat. Centr. delle Gabelle*, 1900.

seed oil, the examination of the unsaponifiable matter by the phytosteryl acetate test should not be omitted. Further information on the detection of cotton seed oil will be given under the headings of " Olive Oil," " Lard," and " Tallow," in this chapter ; and under " Edible Oils and Fats " in Vol. III. Chapter XV.

It has been pointed out already that the finer grades of cotton seed oil are used for edible purposes.[1] The lower grades are employed in enormous quantities as a soap-making oil. On account of its drying and gumming properties cotton seed oil cannot be recommended as a lubricating oil. It is frequently stated that the blown cotton seed oil (see Vol. III. Chap. XV.) is suitable for lubricating purposes ; at any rate considerable quantities of cotton seed oil are converted into blown oil (one brand of such oil is known in the trade as " lardine " [2]) Smaller quantities of cotton seed oil are used as burning oils and in the adulteration of paint oils and for quenching armour plates

Cotton seed oil intended for technical purposes must be " denatured " before importation into Australia either with 5 per cent of its bulk of mineral lubricating oil of specific gravity 86 at 60° F., or 10 per cent of its bulk of mineral lubricating oil of lower specific gravity.

The German Customs prescribe rosemary oil as a denaturant

SESAMÉ OIL, BENISEED OIL, GINGELLI OIL, TEEL OIL

French *Huile de sésame*   German   *Sesamöl*
Italian   *Olio di sesamo.*

For tables of characteristics see pp. 217, 218

Sesamé oil is obtained from the seeds of the sesamé plant, belonging to the family of *Bignoniaceæ* The original home of *Sesamum indicum* is unknown. According to *A de Candolle* sesamé seed was brought from the Sunda Islands to India several thousand years ago, and has migrated thence through the Euphrates basin to Egypt [3]

Linnæus differentiated two species, viz *Sesamum indicum*, L., which produces white or yellow seeds, and *Sesamum orientale*, L., which produces dark (red, brown, or black) seeds. *De Candolle* united the two species of *Linnæus* into one, viz. *Sesamum indicum*, of which he discerns three sub-species, viz. : (1) *S. quadridentatum* = *S. indicum*, L. ; (2) *S. subdentatum* = *S. indicum*, Sims ; and (3) *S. subindivisum* = *S. orientale*, L.

India produces the largest amount of varieties ; there the white seed, yielding the best Indian oil, is termed *suffet-til*, whilst the black variety, containing the largest proportion of oil, is known as *tillie*. In the trade a mixture of white and dark seeds bears the name *bigarré*.

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[1] Such oil has been recommended as a basis for ointments in place of lard (" Adeps gossypii ").

[2] Not to be confounded with the edible fat " lardine " (see Vol. III. Chap. XV.)

[3] Marco Polo mentions already the manufacture of sesamé oil by expression of the seed in Abyssinia, Ceylon, and the Malabar Coast

* According to the rules of the trade, the white sesamé must contain at least 85 per cent of white seeds. If the proportion of dark seed exceeds 15 per cent, an allowance is made. If the dark seed exceeds 25 per cent, the term white sesamé seeds no longer applies.

The *bigarré* quality must contain at least 35 per cent of white seeds. The commercial seed known as "*grosses graines*" must not contain more than 20 per cent of "*petites graines.*" No more than a maximum of 50 per cent of small seeds is permitted ; if they make up from 20 per cent to 50 per cent, an allowance must be made.

By far the largest quantity of *Sesamum indicum* is grown in East India, Java, Siam, Tonkin, China, and Japan.[1] Large quantities are also grown in the countries bordering the Mediterranean, especially in the Levant and Egypt. The seed grown in Africa belongs to the species *Sesamum radiatum*, Shum and Thonn.

Smaller quantities are produced in Algeria and on the West Coast of Africa, as also on the East Coast (Mozambique, Zanzibar, German East Africa). In Southern Rhodesia the seed is cultivated by the natives ; it is not unlikely that in the near future it may be exported to Europe.

In South America the plants are grown in Brazil, Venezuela, and Mexico. In the southern states of North America, and in several islands in the West Indies, the cultivation of the plant appears to be on the increase.

Marseilles has become one of the chief emporia [2] for the production of all grades of sesamé oil from the Levant, the Indies, and West Africa. (It is noteworthy that the first Indian seeds from Bombay were imported into Marseilles by *Schloesing Frères* in the year 1879.) The following table giving the imports of sesamé seed into Marseilles shows the growth of this industry :—

		Kilogs.	
1834	.	601	
1835	.	632	
1841	.	1,608,200	
1842	.	12,108,400	
1843	.	17,963,400	
1850	.	25,729,500	
1855	.	34,021,500,	of which 15,970,300 from Levant, and 19,051,200 from the "Indies."
1870	.	77,803,000,	of which 12,878,000 from Levant, and 64,925,000 from the "Indies."
1901–5	.	295,000,000	
1906–11	.	243,000,000	

The value of the Indian export is given in the following official table :—

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[1] Cp. P. H. Eberhardt, *Le sésame de l'Extrême-Orient*, or *L'Agriculture pratique des Pays Chauds*. Paris, 1911.

[2] The following brands of sesamé seed are known in the Marseilles market :—Red Kundwa (Punjab) ; Bombay mixed ; Red Jubbalpore (Punjab) ; Brown Guzerat ; Black Cawnpore ; Black small Kutnee ; Black Dhera ; White Kauri ; Black Hurda ; Red bold , Black Bellary (Bombay Presidency) ; White Bombay bold ; Kandeish (Bombay Coast) white ; Bombay mixed ; Brown Delhi.

Export of Til, Jinjili, or Sesamé Seed, from East India

Countries.	1899–1900 £	1900–1 £	1901–2 £	1902–3 £	1903–4 £	1904–5 £	1905–6 £	1906–7 £	1907–8 £	1907–8 Cwts.	1908–9 £	1908–9 Cwts.	1909–10[2] £	1909–10[2] Cwts.
France	730,782	499,513	719,533	1,167,245	819,815	482,709	394,991	647,924	422,304	594,225	374,946	588,285	765,776	1,315,889
Austria-Hungary	43,661	52,076	34,360	94,581	135,985	84,421	53,535	114,578	150,844	215,557	246,915	374,182	248,107	414,222
Belgium	127,424	225,151	355,670	325,361	367,580	261,231	351,917	535,457	399,006	401,234	171,236	258,668	441,662	723,723
Italy	106,524	166,520	111,511	158,953	74,351	132,779	17,593	97,112	61,479	90,681	128,725	197,549	115,315	192,098
Germany	126,914	100,640	114,413	141,948	118,365	88,802	103,728	190,208	131,839	172,679	103,760	152,331	145,201	240,726
Egypt									32,324	43,965	41,651	66,277	30,794	49,532
United Kingdom									432				6,553	14,089
Other Countries	94,662	45,338	34,593	54,386	113,200	106,172	57,739	95,865	19,500	29,180	16,839	25,997	5,048	8,556
Total	1,139,972	1,035,238	1,429,291	1,939,574	1,619,296	1,156,113	979,536	1,691,904	1,127,818	1,552,472	1,084,072	1,657,292	1,758,456	2,958,829

[1] Earlier exports were as follows:—

	Tons
1891	1847
1892	2302
1893	270
1894	424
1895	235
1896	1800
1897	1790
1898	275

[2] The total 1909–1910 crop amounted to 516,000 tons.

The acreage of land under sesamé cultivation in India is given officially as follows :—

	Average Area during 1899-1909	Average Yield during 1899-1909
	Acres	Tons
United Provinces { Pure	292,900	25,500
United Provinces { Mixed	700,000	60,000
Central Provinces and Berar	918,000	67,900
Madras	460,000	38,000
Bombay [1]	861,900	107,600
Bengal	250,200	29,800
Punjab	148,500	14,100
Sind [2]	92,500	6,300
Hyderabad	484,000	..

[1] Including Native States.   [2] Excluding Hyderabad.

The following tables specify the imports of sesamé seed into France and Marseilles from the Levant, India, and China   The totals include the seed from West Africa :—

Imports of Sesamé Seed into France and Marseilles

France.   Metric tons

Year	The Levant	India	China	Total
1900	6,768	56,660	5,384	69,689
1901	5,531	61,353	4,899	73,791
1902	5,467	65,188	10,670	83,413
1903	3,375	121,453	7,920	138,266
1904	4,197	96,175		101,617
1905	3,357	48,198	2,666	55,172
1906	6,877	30,708	20,991	61,194
1907	4,898	59,390	3,216	71,420
1908	2,267	25,085	26,183	54,783
1909	1,671	39,662	21,125	63,620
1910	718	91,393	10,682	105,556
1911	884	65,587	32,371	101,984

[TABLE

Marseilles.   Metric tons

Year.	The Levant	India.	China.	Africa	Bussorah.	Total.
1896	11,416	62,568	97	..	..	76,021
1897	12,843	33,475	..	..	..	49,411
1898	7,236	53,802	..	..	..	61,627
1899	3,755	64,013	893	..	..	66,090
1900	6,618	53,185	4,834	..	.	65,462
1901	4,555	54,454	4,899	..	..	65,573
1902	5,108	56,357	9,898	..	..	73,367
1903	3,375	110,782	6,649	..	..	123,324
1904	4,497	88,770	..	..	..	94,225
1905	3,255	44,097	2,512	830	10	50,704
1906	6,777	28,213	10,171	1408	1281	47,850
1907	4,485	54,959	2,575	1472	346	63,837
1908	324	17,470	21,818	1405	732	41,749
1909	1,772 [1]	40,852	20,290	1044	129	64,087
1911	..	24,846	320	3068	..	28,518

The importance of China as a supplier of sesamé seed is growing yearly, as may be gathered from the statistical data contained in the preceding tables.

The earlier total exports were as follows :—

Year.	Tons.
1894	138
1895	238
1896	40
1897	54
1903	631
1904	154

In the year 1909 the total export of sesamé seed from China to foreign countries amounted to 128,165 tons, valued at £1,520,021.[2]

The chief European ports to which Chinese seed was shipped and the quantities are given in the following table :—

Name of Port	Quantity (cwts.)
Rotterdam	690,640
Marseilles	404,660
Trieste	301,400
Genoa	242,500
Antwerp	230,560
Hamburg	177,470
Bremen	134,900

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[1] The total of 1772 tons has been supplied as detailed in the following table :—

	Tons.
From Jaffa, Caiffa, St. Jean d'Acre	1601
„ Tarsus	116
„ Smyrna, Echelle-Neuve, Salallah	29
„ Enos, Gallipoli	11
„ Volo, Salonica	15
	1772

[2] Bull. Imp. Inst., 1911, 267.

The following statistics show the exports from the Anglo-Egyptian Sudan and German East Africa :—

Value of Sesamé Seed Exports from the Anglo-Egyptian Sudan [1]

Year.			Value (£).
1902	.	.	4,977
1903	.	.	2,583
1904	.	.	522
1905	.	.	5,787
1906	.	.	3,705
1907	.	.	19,736
1908	.		25,084
1909	.	.	63,066

Value of Sesamé Seed Exports from German East Africa [1]

Year.			£.
1904	.	.	18,701
1905	.	.	10,423
1906	.		5,658
1907	.	.	6,290
1908	.	.	9,650
1909	.	.	14,200
1910	.	.	10,590

The quantities exported from 1892 to 1897 were on the average 21 tons only.

The sesamé oil industry has not been able to obtain a foothold in Great Britain, inasmuch as the finer qualities of sesamé oil obtained in the first expression do not find so remunerative an outlet as they do in other countries ; in fact, the whole of the oil would have to be disposed of as soap oil.

The small amount of seed imported into this country is used in the manufacture of compound cake, the high proportion of oil in sesamé seed helping to bring up the percentage of oil in the mixed meal to the legally prescribed amount.

Since the admixture of sesamé oil to margarine has been made obligatory in Germany, Austria, and Belgium, a considerable sesamé oil industry has rapidly sprung up in these countries. The figures for Germany and Austria are given in the following tables :—

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[1] *Bull. Imp. Inst.*, 1911 268.

Imports of Sesamé Seed into Germany

Year.	Total.	From					
		East Indies.	China	East Africa		The Levant	Mexico.
	Double cwts	Double cwts	Double cwts	Double cwts		Double cwts	
1896	232,530	187,910				28,570	
1897	210,240	186,740	...	...		10,120	
1898	312,330	267,470	...	...		24,520	
1899	387,710	364,180	. .	...		8,900	
1900	296,370	261,030	14,410	1131		8,185	
1901	358,700	309,950	14,930	3945		21,128	
1902	498,180	373,120	91,560	4537		11,228	
1903	615,380	427,160	166,730	2234		3,612	
1904	513,130	469,960	15,790	5416		16,252	
1905	464,892	331,700	.	.		...	
1906	573,810	319,380	202,300	...		42,540	
1907	668,250	581,108	47,510	...		33,110	
1908	729,690	...	...	...		...	
1909	779,400	...	...	...		...	
1910	1,413,970	...	...	...		...	
				German	Portuguese.		
1911	1,016,721	331,297	653,220	8279	4740	nil	nil
1912	992,818	196,502	759,385	6587	8835	nil	5635

Imports of Sesamé Seed into Austria [1]

Year.	Kilogs
1900	13,288,500
1901	15,439,900
1902	12,608,200
1903	31,793,300
1904	36,767,400
1905	15,491,400
1907	19,520,100
1908	17,375,100
1909	42,802,000
1910	39,491,800
1911	42,199,700

In the years 1911 and 1912 Germany imported 393 and 280 tons of oil respectively from Belgium, and 388 and 266 tons from France.

Sesamé seed belongs to the oleaginous seed which is rich in oil, hence it must be subjected to repeated expression. The proportion of oil varies from 50 to 57 per cent. From the following table, due to *Sprinkmeyer and Wagner*,[2] it would appear that African seed contains more oil than Indian, but a much more extended series of experiments is required to

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[1] Cp. also table p 210.
[2] *Zeits. f. Unters. d Nahrgs- u. Genussm.*, 1905, x. 353.

justify general conclusions. The table proves further the correctness
of the general experience that ether extracts larger quantities of oil
from the seeds than does petroleum ether

Extracted with	Indian Seed,	Levant Seed	African Seed
	Per cent,	Per cent	Per cent,
Ether .	49 76	50·14	54·14
Petroleum ether .	47·57	47·57	52·54

The following table gives the *practical yields* obtained on a large
scale by the expression of seeds from various countries   The seeds
were pressed once or twice in the cold, and then once in the hot.

Practical Yields from Sesamé Seed

Description of Seed	Per cent.
Bombay seed, yellow or red	14-15
Bombay seed, bigarré	12 11
Levant seed	17-18
Chinese seed	44-45

The oils of the first expression in the cold represent the best qualities.
    The finest edible sesamé oil is obtained from the Levant seeds.
Of these the Jaffa district yields the best brand.   Slightly inferior in
flavour to the Jaffa oil are those obtained from seed grown in Caiffa,
St Jean d'Acre, Tarsus, Smyrna, Mersyna.   The oil from Alexandretta
seeds represents a lower grade still   The Indian seeds, embracing chiefly
those from Kurrachee and Bombay, give oils of more unpleasant
flavour, and are therefore not suitable for the *best kinds* of margarine.
Lower still as regards taste and flavour rank the oils from Chinese
and African seeds   In China the seeds are roasted before being ground
and expressed in wedge presses.   Owing to this process the oil becomes
dark-coloured and acquires a strong flavour of nuts

The oils of second and third expression are used for manufacturing
purposes, chiefly for soap-making.

The press cakes contain from 8 to 10 per cent of oil , they form an
excellent cattle food, and are largely in demand for this purpose

The average composition of sesamé cake is the following : -

Oil	14·63
Moisture	7·65
Proteins	36 14
Ash	13·17 [1]
Crude fibre	4·83
Carbohydrates .	23 58
	100·00

[1] Cp. Linseed cake, p. 59,

When the seed does not arrive in the sound state in which it is obtained at present almost regularly, the cakes resulting from such unsound seeds are unsuitable [1] for feeding cattle, and are therefore extracted with solvents for the complete recovery of the oil. The extracted meal is then sold as a manure, greatly appreciated by the farmer on account of its fertilising properties. *Bang and Sanguinetti* of Marseilles [2] devised a special apparatus for the extraction of sesamé seed with petroleum ether. At present, damaged seed is extracted with carbon bisulphide. In 1903 about twenty thousand tons of press cakes were thus extracted in Marseilles, yielding about two thousand tons of oil. In 1905 only twelve thousand tons of cakes, yielding about one thousand tons of oil, were extracted. The oil so obtained is white or dirty grey. At the ordinary temperature some " stearine " deposits, hence extracted sesamé oil represents a more or less pasty mass. Owing to the damaged state of the seed the oil contains a notable proportion of free fatty acids. For the manufacture of mottled soaps the extracted oil can be used as such. If intended to be used as burning oil or for lubricating purposes, the free fatty acids must be first removed.

Sesamé oil contains, according to *Farnsteiner*, 12·1 per cent to 14·1 per cent of solid acids ; *Lane* [3] obtained by the lead-salt-ether method 78·1 per cent liquid fatty acids. These consist of oleic and linolic acids. Direct determination of linolic acid (by means of the linolic tetrabromide) gave 16·4, 15·2, and 12·6 per cent linolic acid. From the composition of 12·1 per cent solid acids, 15·8 per cent linolic acid, and 72·1 per cent of oleic acid, there would be calculated as the iodine value of the mixed fatty acids 93·6, whereas direct determination gave the mean value of 111. According to the above-given composition the liquid fatty acids would consist of 82 per cent of oleic acid, and 18 per cent linolic acid. This would lead to 106·4 as the calculated iodine value of the liquid fatty acids, whereas direct determinations have given the mean figure of 133. Also this calculation (cp. Cotton Seed Oil) shows that the linolic tetrabromide has not been fully recovered. More recent determinations of linolic acid carried out in the author's laboratory have been detailed (Vol. I. Chap. VIII.).

Sesamé oil is dextro-rotatory, a property which may supply a useful additional means of identifying the oil. The numbers ascertained by *Bishop* have been given above (Vol. I. Chap. V.). *Utz* [4] found the rotations of three specimens of African, Indian, and Levant oils in a 200 mm. tube at 15° C. +1·6°, +1·4°, and +0·8° respectively. *Spinkmeyer and Wagner* confirm that the African oil has the highest rotation, whereas they find the lowest rotations in Indian oils. It should, however, be noted that only in the absence of castor, croton, and rosin oils would the polarimetric observation be of any value. The optical activity of the oil is no doubt due to the presence of phytosterol and sesamin (see below).

[1] Possibly it is to such unsound seed that the poisonous properties of some sesamé oils, noticed recently (No. 43 *Berliner Klinische Wochenschrift*, 1906), must be ascribed.

[2] Austrian patent, 5th July 1883.

[3] *Journ. Soc. Chem. Ind.*, 1901, 1083.

[4] *Pharm. Zeit.* 45, 490 , *Journ. Soc. Chem. Ind* , 1900, 914.

Physical and Chemical Characteristics of Sesamé Oil

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Thermal Tests		Refractive Index		
At °C.	Observer	°C.	Observer	Mgrms. KOH	Observer	Per cent.	Observer	Maumené Test		At °C.	Degrees	Observer
								Observer				
15	0.9230-0.9237 De Negri and Fabris	-4 to -6	De Negri and Fabris	188.5-190.4	De Negri and Fabris	106.9-107.8	De Negri and Fabris	°C.	Archbutt	15	1.4748	Strohmer
											1.4762	Harvey
								65	De Negri and Fabris	20	1.4728	Thorner
15.5	0.924-0.926 Shukoff[1]			102-103	Thorner	103-105	Thorner	63-64	Suzzi	60	1.4561	
15.5	0.9203 Boley[2]			188-190	Shukoff[1]	114-115	Shukoff[1]				Oleo-refractometer.	
20	0.917-0.9210 Wijs[3]					106.1-114.5	Wijs[5]	70.9			"Degrees."	Observer.
35	0.9078-0.9098 Long					105.2-110.3	Wijs[6]	72.5			-17 to +18	Jean
						103.9-109.8	Wijs[7]	Heat of Bromination.			+13 to +17 at 22°C.	Pearmain
								°C.	Observer.		Butyro-refractometer.	
								23- 23.9	Bromwell and Meyer	At °C.	"Degrees"	Observer.
						114.4	Sprinkmeyer and Wagner			25	68-68.2	Sprinkmeyer and Wagner
						104.2.2	Suzzi			27	69.2.4	
						108.9.10				40	59.6-60.8	
										40	40.6.4	

1 Russian oils. 2 Finest Jaffa oil, determined in the author's laboratory. 3 One specimen (from Curaçao seed) had the specific gravity 0.920
4 African oil. 5 One specimen (from Curaçao seed) had the iodine value 116. 6 Oils of second expression
7 Oils of third expression 8 Indian and Levant oils
9 Oil from Erythrean (Italian East Africa) bizarre seed 10 Oil from Erythrean (Italian East Africa) white seed

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Solidifying Point		Melting Point		Neutralisation Value		Mean Molecular Weight		Iodine Value		Refractive Index	
Per cent.	Observer	°C.	Observer	°C	Observer	Mgrms KOH	Observer		Observer	Per cent.	Observer	At 60° C.	Observer
95·8	Bensemann	18·5 25-26	Allen Bensemann [1]	23 29-30	Allen Bensemann [2]	199·3 201·6	Valenta Thorner	286	Valenta	108·9-111·4	Mojawski and Demski	1·4461	Thorner
		20-22	De Negri and Fabris	24-26	De Negri and Fabris	196·07	Suzzi			111·8-112	De Negri and Fabris	Butyro-refractometer.	
		23·5	Thorner	25-32	Thorner					110-111	Thorner	°C "Degrees." Observer	
		Titer Test.	Lewkowitsch							Liquid Fatty Acids		25|53·2-54 40|45·1-47·2 25|55·4-56·5	Utz " Sprinkmeyer & Wagner
		22·9-23·55 23·7-23·8 21·5-22·93	Lewkowitsch " "							189·9 130·9-136·3 [3] 129·4 [4] 129·5	Lane Tortelli and Ruggeri " Lewkowitsch	"|54-55 [6] 40|47·2- 47·7 [5] "|45·5- 46·8 [6]	" " "

[1] Point of incipient fusion.　　2 Point of complete fusion.　　3 Iodine value of oil, 108·6-113·7.
4 Jafla oil; iodine value of oil, 109·5.　　5 African oil.　　6 Indian and Levant oils.
7 Saponification value, 198·3.

The amount of unsaponifiable matter in sesamé oil varies from 0·95 per cent to 1·32 per cent. The unsaponifiable matter contains phytosterol, sesamin, and a " red oil " (see below). The phytosterol was identified by the melting point of the crystals obtained by crystallising it seven times from alcohol. *Siegfeld* [1] thus prepared a phytosterol of the melting point 139·0 – 139·2° C. The phytosterol acetate obtained by *Bomer* melted at 128°-129° C. *Siegfeld* prepared crystals melting at 130°-131° C. by recrystallising the acetate seven times. According to *Tocher* [2] glacial acetic acid extracts from sesamé oil two substances—

(a) A resinous substance forming long crystalline needles (from alcohol), melting at 118° C. From ultimate analyses and determinations of the molecular weight (by *Raoult's* method in benzene and acetic acid) the formula $C_{18}H_{18}O_5$ was derived. This substance was named *sesamin*. Sesamin does not give the *Baudouin* test (see below), but assumes a green and then a bright red colour with nitro-sulphuric acid (the colour reaction given by the U.S. Pharmacopœia for sesamé oil).

(b) A thick brown oil (of unknown composition) giving the characteristic colour reactions of sesamé oil.[3]

Villavecchia and Fabris [4] found that by extracting the oil itself with either acetic acid or alcohol the chromogenetic substance cannot be wholly removed. By converting the oil into barium soap, and extracting the latter with alcohol, they isolated from the alcoholic extract, after evaporating off the alcohol, and dissolving the residue in petroleum ether, three substances—

1. An alcohol of the melting point 137° C., and rotatory power $[a]_D^{20} = -34° 23'$ (for $c = 5·013$). This alcohol is doubtless sitosterol; it is not accompanied by stigmasterol (*Klamroth* [5]).

2. Fine crystals having the formula $(C_{11}H_{12}O_3)_2$ and melting at 123° C. (*Villavecchia and Fabris*); according to *Bomer and Winter* their formula is $C_{33}H_{30}O_{10}$, and they melt at 122·5° C. The rotatory power is $[a]_D = +68·36$ (for $c = 24·45$) in chloroformic solution. This substance was termed *sesamin* by *Villavecchia and Fabris*. It is apparently identical with *Tocher's* sesamin $C_{18}H_{18}O_5$, for theory requires for $C_{18}H_{18}O_5$, C = 68·79 per cent, H = 5·73, and for $C_{11}H_{12}O_3$, C = 68·75, H = 6·25, and for $C_{33}H_{30}O_{10}$, C = 67·54 per cent, H = 5·17 per cent. *Tocher* found (by *Raoult's* method) the molecular weight of sesamin 311 (in benzene) and 312 (in acetic acid). *Villavecchia and Fabris* [6] obtained (by *Raoult's* method) the molecular weight 350 (in benzene), the formula $(C_{11}H_{12}O_3)_2$ demanding 384; *Bomer and Winter's* proposed formula $C_{33}H_{30}O_{10}$ leads to a molecular weight of 586. Sesamin is sparingly soluble in ether and can thus be separated from cholesterol.[5]

3. A thick, non-crystallisable oil, free from nitrogen. This oil

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1901, 585

[2] *Pharm. Journ. and Trans.*, 1891, 639 ; 1893, 700.

[3] *Merkling's* (*Journ. Soc. Chem. Ind.*, 1888, 45) statement that it is the glacial acetic acid extract which gives the characteristic colour reaction of sesamé oil must therefore be corrected.

[4] *Journ. Soc. Chem. Ind.*, 1891, 69.

[5] Klamroth, *Inaug. Dissert*, Munich, 1911.

[6] *Annali del Lab. Chim. delle Gab.*, 1897 (in.), 22

contains the substance minute quantities of which produce the characteristic colour reaction with sugar and hydrochloric acid (see below) ; this oil seems to be identical with *Tocher's* substance (*b*). It should be noted that the chromogenetic substance entirely passes into the liquid fatty acids, if the latter be prepared by the lead-salt-ether method, in contradistinction to those olive oils (see below) which simulate sesamé oil in the *Baudouin* test (*Tortelli and Ruggeri* [1]).

The last-mentioned **colour reaction** is extremely characteristic of sesamé oil, so that it can thereby be detected with certainty in mixtures with other oils. This test, due to *Camoin*—generally, however, known as the *Baudouin* reaction—is the only colour reaction which has hitherto been found absolutely reliable in the examination of natural oils and fats.[2] It is all the more valuable as the chromogenetic substance is not destroyed by heating the oil to 250° C. for twenty minutes (*Tortelli and Ruggeri*). Nor can it be removed by filtering the oil over charcoal, as the author has ascertained by special experiment. On reducing sesamé oil with hydrogen in the presence of a catalyst, the chromogenetic substance is frequently affected (cp. Vol. I. Chap. VII. p 497).

Baudouin's test is usually carried out in the form recommended by *Villavecchia and Fabris* :—Dissolve 0·1 grm. of sugar in 10 c.c. of hydrochloric acid of spec. grav. 1·19 in a test-tube, add 20 c.c. of the oil, shake thoroughly for one minute and allow to stand. The aqueous solution separates almost immediately ; in the presence of even the smallest quantity of natural sesamé oil it will be found coloured crimson.

Villavecchia and Fabris attribute the chromatic reaction to the agency of levulose, or of substances produced by the action of hydrochloric acid on the latter ; therefore glucose, maltose, and galactose cannot be used in place of saccharose. The main product of the interaction of levulose and hydrochloric acid being furfural, the latter can accordingly be substituted for the mixture of sugar and hydrochloric acid. Inasmuch as furfural itself gives a violet tint with hydrochloric acid, it is necessary to use a dilute solution ; it has been found best to employ a 2 per cent alcoholic solution of furfural. The modified test is carried out in one of the following two forms :—

(*a*) Place 0·1 c.c. of a 2 per cent furfural solution in a test-tube, add 10 c.c. of the oil, and 10 c.c. of hydrochloric acid of spec. grav. 1·19, shake the mixture for half a minute and allow to settle. In the presence of sesamé oil, even if it be less than 1 per cent, the aqueous layer will acquire a distinct crimson colour. In the absence of sesamé oil the lower layer is either colourless, or has at most, as in the case of a very rancid though pure olive oil, a dirty yellow colour.

(*b*) Mix, as above, 0·1 c.c. of the alcoholic furfural solution with 10 c.c. of the oil, and add 1 c.c. only of hydrochloric acid, agitate thoroughly and induce separation by addition of 10 c.c. of chloroform, when the aqueous layer will float on the top. Even less than 1 per

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[1] *Chem. Zeit.*, 1898, 601.

[2] With regard to the detection of sesamé oil in edible fats in the presence of "butter colours" by means of this reaction see "Butterfat."

cent of sesamé oil is indicated by the crimson colouration of the aqueous layer.

In comparative tests it is important to use little furfural and strong hydrochloric acid.

These two methods have been tried with a large number of olive and arachis oils obtained from various localities, and further rape (colza), cotton seed, linseed, walnut, poppy seed, neat's foot, blubber, and fish oils, and their complete reliability has been confirmed.[1] With regard to olive oils it should be noted that some Tunisian, Algerian, and Portuguese olive oils from Douro (*Domergue, Burker, Ferreira da Silva*), as also some Italian olive oils (*Lalande and Tambon*) from the province of Bari, Brindisi, and Lecce, give a colour reaction which may create a doubt. In such cases *Milliau* relies on the colour test given by the fatty acids. Also *Tortelli and Ruggeri*[2] recommend to test the liquid fatty acids, since the chromogenetic substance of such abnormal olive oils does not pass into the liquid fatty acids. Thus, distinction between such olive oils and olive oils adulterated with sesamé oils is rendered feasible.

Hitherto the author has not met with a sample of sesamé oil that failed to give the *Baudouin* reactions, although his experience with sesamé oil extends over a large number of years and embraces all commercial varieties of sesamé oils, both of edible and of commercial quality.

It may, however, be pointed out that *Partheil*[3] failed to obtain the colour reaction with a sesamé oil extracted by means of chloroform from sesamé cake, and that *Weigmann*[4] and also *Soltsien*[5] met with similar failure in the case of rancid sesamé oil. The same exceptional observation has been made by *Lauffs and Heismann*.[6] Curiously enough the last-mentioned observers did obtain the *Baudouin* reaction on adding cotton seed oil ; hence their statement requires revision.[7]

It should be pointed out that some colouring matters which are used legitimately for colouring butter and margarine give with hydrochloric acid alone a reaction similar to that obtained in the *Baudouin* test. This is of special importance for the detection of sesamé oil in margarine, and in butter adulterated with margarine containing sesamé oil. Some of these colouring matters can be readily removed by washing the fat with hydrochloric acid ; others, however, require so persistent and repeated a treatment with hydrochloric acid that finally the chromogenetic substance in sesamé oil is destroyed and the furfural test cannot be obtained, even if sesamé oil be present (cp. Chap. XIV. " Butter Fat ").

To meet such cases the *Soltsien* test—colouration on treating with

[1] Further confirmation is given by Wauters, *Journ. Soc. Chem. Ind.*, 1896, 136.

[2] *Chem. Zeit.*, 1898, 601.

[3] *Zeits. f. angew. Chem.*, 1898, 730.

[4] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1901, 131.

[5] *Ibid.*, 1906, xii.

[6] *Chem. Zeit.*, 1907, 1023.

[7] Cp. Sprinkmeyer, *Zeits. f. Unters. d Nahrgs- u. Genussm.*, 1908 (xv.), 21. Kreis, *Chem. Zeit.*, 1908, 87. Utz, *Chem. Revue*, 1908, 112.

Bettendorff's reagent [1]—has been recommended. As this test is prescribed officially in Germany it may be given here. According to the official directions [2] 5 c.c. of the sample are dissolved in a test tube in 10 c.c. of petroleum ether and 2·5 c.c. of a strongly fuming stannous chloride solution.[3] The mixture is thoroughly shaken, so that a homogeneous mixture results, but not longer, and immersed in water of 40° C. After the stannous chloride solution has separated out, the test tube is placed in water at 80° C. in such a manner that only the stannous chloride solution becomes warm and the petroleum ether layer does not commence to boil. In the presence of sesamé oil the stannous chloride solution is stated to show after warming for 3 minutes a distinct red colouration.

The author is unable to recommend this test and may add that if applied to rancid sesamé oil it always fails. Moreover, fat extracted from cakes, etc., prepared with pure butter, always furnishes a red colouration [4] This experience agrees with the view that the chromogenetic substance producing the *Baudouin* test is not identical with the substance acting in stannous chloride.

Considering the reliability of the *Baudouin* reaction, all " modifications," and other colour reactions that have been proposed and are still being proposed, are of no importance. Therefore they are omitted in this treatise.[5]

Kreis [6] detected in sesamé oil a new substance, which he considers to be a phenol, as it combined with diazo compounds; hence it was termed " sesamol." According to *Malagnini and Armanne* [7] sesamol does not occur in the free state in sesamé oil, but as a complex body from which " sesamol " is set free on adding a mineral acid.

The drying power of sesamé oil is much less pronounced than that of cotton seed oil. In the *Livache* test, after seven days only 2·4 per cent of oxygen were absorbed; under the same conditions the fatty acids absorbed 2 per cent of oxygen after eight days.

In the elaidin test sesamé oil becomes red after a short time, and

[1] With regard to this test see Polenske, *Arb. a. d Kais. Gesundheitsamt*, 1905, 570 ; Sprinkmeyer und Wagner, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905, x. 348 , Fendler, *Chem. Revue*, 1905, 10 , Soltsien, *Chem. Revue*, 1906, 138 ; Gerber, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiii. 67.

[2] " Entwuerfe zu Festsetzungen ueber Lebensmittel," herausgegeben vom *Kaiserl. Gesundheitsamt*, Heft 2 , Speiselette und Speiseoele, Berlin, 1912.

[3] The stannous chloride solution is prepared by mixing 5 parts of crystalline stannous chloride with 1 part (by weight) of hydrochloric acid and saturating completely with dry hydrochloric acid, allowing to separate, filtering through asbestos and keeping in small stoppered bottles which should be kept completely filled.

[4] E. Hofstadter, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909, xvii. 436.

[5] Cp. 2nd ed. of this work, pp. 391, 392. Belber, *Ann. chim. analyt. appliq.*, 1899, 217. Bomer, *Zeits f. Unters. d Nahrgs- u. Genussm.*, 1899, 705. Brenl, *Chem. Zeit.*, 1899, 617 ; Vandevelde, *Bull. de l'Ass. Belge*, 1900, May. Kreis, *Chem. Zeit.*, 1902, 1011 ; 1903, 316, 1030. Tambon, *Journ. Pharm et Chim.*, 1901, 57. Utz, *Chem. Revue*, 1902, 177 ; *Journ. Soc. Chem. Ind.*, 1902, 1196. C. Fleig, *Bull. Soc. Chim de France*, 1908, 984. M. Labat, *Bull. Soc. Pharm. Bordeaux*, 1908 (July).

[6] *Chem. Zeit.*, 1903, 1030.   [7] *Ibid.*, 1907, 885.

acquires a dirty reddish brown colour, yielding even after only twenty-four hours' standing a semi-fluid claidin.

By reduction with hydrogen in the presence of a catalyst sesamé oil is converted into a hard fat of any desired iodine value according to the treatment (see " Hydrogenised Fats," " Hardened Fats," Vol. III. Chap. XV.).

Paal and Roth[1] obtained by catalytic reduction with palladium a slightly yellowish brittle mass conglutinating at 59° C. and melting at 69° C., which absorbed 4·2 per cent of iodine This product gave the *Baudouin* reaction only very faintly. On reducing the product of the iodine value 4·2 for a second time a product melting at 65°-69° C and absorbing 2 per cent of iodine was obtained. The *Baudouin* reaction was fainter still than that of the reduced product which absorbed 4·2 per cent of iodine. After keeping the solid fat of the iodine value 2 for 8 months the *Baudouin* reaction had become more intense although it did not reach the intensity of the original oil.

The cold-drawn sesamé oil is largely used as an edible oil, notably in the manufacture of margarine. Since small quantities of sesamé oil are easily revealed by the *Baudouin* test, it has been made obligatory in Germany and Austria to use at least ten parts of sesamé oil in the manufacture of margarine for 100 parts of fatty matters (cp. "Margarine," Vol. III. Chap. XV.). In Belgium 5 per cent are prescribed. The finest sesamé oils are consumed as table oils ; small quantities of this class of oil are used in the production of perfumes (" enfleurage "). Sesamé oil finds employment in perfumery (for the extraction of balsam of Peru, sandalwood, etc.).

The best cold-drawn oil being rather high in price, adulteration of the best qualities with poppy seed oil, cotton seed oil, and arachis oil is not infrequent. The sesamé oils of second and third expression are frequently adulterated with rape oil.

Poppy seed oil is detected by a higher iodine value than the normal one. For the detection of *cotton seed oil* the melting and solidifying points of the fatty acids should be determined. The iodine value of an *oil* suspected of being adulterated with cotton seed oil would not afford certainty. The iodine value of the liquid fatty acids, as also the determination of the tetrabromide, carried out under the conditions described in Vol. I. Chap. VIII., would furnish more reliable data As confirmatory tests, the colour reactions of cotton seed oil described above should be resorted to.

Arachis oil is detected by the isolation of arachidic acid. The addition of arachis oil would lower the specific gravity of the sample.

The presence of rape oil would be ascertained by a low specific gravity of the sample, low solidifying and melting points of the fatty acids, and notably a low saponification value. In important cases the detection of behenic acid obtained by catalytic reduction of erucic acid would be required (see Vol. I. Chap. VIII. p. 553).

Sesamé oil is in its turn used as an adulterant of fatty oils, notably of poppy seed oil. Admixture of sesamé oil with other oils is, however,

[1] *Berichte*, 1909, 1550.

little practised, since the detection of the smallest quantity of sesamé oil is rendered easy by the *Baudouin* test.

The lower qualities of sesamé oil find a large outlet for soap-making in the south of Europe and are especially used in the manufacture of the Marseilles mottled soap (cp. Vol. III. " Soap Manufacture ") ; they are also used as burning oil and for making india-rubber substitutes. A speciality of the Marseilles trade is the employment of oil extracted from damaged seeds with carbon bisulphide [1] in the soap industry. Such extracted oil is now being exported to Germany.

BASSWOOD OIL [2]

French—*Huile de bois de tilleul.* German—*Lindenholzol.*
Italian—*Olio di legno di tiglio.*

This oil is obtained from basswood (*Tilia americana,* L.) (a tree widely distributed in America from Virginia to the Alleghany mountains, in Georgia, Nebraska, and Kansas) by extracting the rasped *wood* with ether.

Physical and Chemical Characteristics of Basswood Oil

Specific Gravity	Solidifying Point	Saponific Value.	Iodine Value
At 15° C. (Water 15° C. =1)	°C.	Mgrms KOH.	Per cent.
0·938	− 10	178·1	111

The seeds from *Tilia parvifolia* (= *Tilia cordata,* Mull.) yield an oil, the characteristics of which will be given below in the table headed " Lesser known semi-drying-oils."

LEMON PIPS OIL

French— *Huile de pepins de citrons.* German—*Citronenkernol.*
Italian—*Olio di semi del limone.*

Lemon pips oil is obtained as a pale yellow oil having a bland flavour recalling that of almond oil, by extraction of dried and ground lemon pips with solvents.

A specimen examined by *Peters and Frerichs* [3] had the saponification

[1] Boutoux, *Les Matières Grasses,* 1910, 1857.
[2] Weichmann, *Journ. Soc. Chem. Ind.,* 1895, 665.
[3] W. Peters and G. Frerichs, *Arch. d. Pharm.,* 1902 [240], 659, *Journ. Soc. Chem. Ind.,* 1903, 102.

value 188·4 and the iodine value 109·2.   The acetyl value of the sample
is given as 13·65.

The fatty acids are stated to consist of palmitic, stearic, oleic, and
linolic acids.

LUFFA SEED OIL, LOOFAH SEED OIL

French—*Huile de luffa*.   German—*Schwammkürbiskernöl*.
Italian—*Olio di luffa*.

Physical and Chemical Characteristics of Luffa Oil

Specific Gravity	Saponification Value	Iodine Value	Reichert-Meissl Value	Refractive Index		Insoluble Acids + Unsaponifiable	Observer.
At 15·5° C. (water at 15·5 = 1)	Mgrms KOH	Per cent	c.c. $\frac{1}{10}$ norm KOH	Butyro-refractometer "Degrees"			
0·9254	187·80	108·51	1·43	62·0 at 40 C.°		94·8	Crossley and Le Sueur [1]
0·924-0·926	193-195·8	..	0·49-0·52	..		93·8	D. Hooper [2]

This oil is expressed in East India from the seeds of *Luffa ægyptiaca*,
Mill., and is used by the natives as an edible oil.   Small quantities of
the seeds are exported from British Nigeria.[3]

The oil examined by *Crossley and Le Sueur* was reddish brown in
colour and had a slight odour.   *Titer* test of the fatty acids, 34°-35° C.
(*D. Hooper*).

MYRTLE SEED OIL [1]

French—*Huile des sémences de myrte*.   German—*Myrtensamenöl*.
Italian—*Olio di semi di mirto*.

The seeds of the common myrtle, *Myrtus communis*, L., contain
12-15 per cent of a fatty oil of characteristic taste and pleasant odour.
The following characteristics have been ascertained :—

Specific gravity at 15° C.	0·9244
Saponification value	199·8
Iodine value	107·5
Reichert-Meissl value	9·65
Insoluble fatty acids + unsaponifiable	95·3 per cent
Maumené test in Tortelli's thermoleometer	39° C.

[1] *Journ. Soc. Chem. Ind.*, 1898, 991.
[2] *Annual Report, Indian Museum*, 1907-1908, p. 15.
[3] *British Nigeria*, by F. A. Mockler Ferryman, p. 318.
[4] Semichon and Perciabosco, *Gazz. Chim. Ital.*, 1907 (37), i. 183.

The saponification value appears to be very low in view of the high *Reichert-Meissl* value. The number given for the *Maumené* test would also appear too low, considering the high iodine value, whereas olive oil (iodine value 83) indicates in *Tortelli's* thermoleometer a rise in temperature of 44° C.

An examination of the fatty acids showed that the oil contains the glycerides of myristic, palmitic, oleic, and linolic acids. No stearic acid was found by *Hehner and Mitchell's* method.

PECAN OIL, PACCAN OIL

This oil is contained in the nuts of *Juglans nigra*, L., a tree largely cultivated in North America. The kernels form 47 per cent of the nuts and contain 70·4 per cent of a light straw-coloured oil, having a pleasant pecan odour and taste.

The oil extracted with ether gave the following characteristics : [1]—

Specific gravity 15/15° C. . .	0·9184
Saponification value .	198·0
Iodine value (Hubl's method) .	106·0
Reichert-Meissl value . .	2·2
Insoluble fatty acids + unsaponifiable . .	93·4

SPINDLE TREE OIL

French—*Huile de bonnet de prêtre.* German—*Pfaffenhütchenöl, Spillbaumöl.* Italian—*Olio di fusaggine.*

Kochs [2] obtained from the arillus and the seeds of the spindle tree (*Evonymus europœa*, L.), 35·2 per cent of a bright reddish-brown oil. This deep colour is due to the colouring matter of the arillus having been extracted. The acid value of the specimen examined by *Kochs* was 84 and the unsaponifiable matter was very high. The oil had the following characteristics :—

Oil—

Specific gravity at 15° C. . . .	0·9390
Solidifying point	– 10° C.
Saponification value . . .	230·1
Reichert-Meissl value . . .	35·31
Butyro-refractometer " degrees " at 40° C. .	52
Unsaponifiable matter	5·83 per cent

Fatty Acids—

Melting point—commences to melt at .	38° C.
„ „ completely melted at .	70° C.
Iodine value	105·3
Neutralisation value . . .	223·6

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[1] A. C. Deiler and G. S. Traps, *Amer. Chem. Journ.*, 1910 (43), 90.

[2] *Jahresb. d. Versuchs. d. k. Gartnerlehranst.*, Dahlem, 1906–1907.

The exceedingly high saponification and *Reichert-Meissl* values would seem to confirm the statement (Vol. I. Chap. III.) that the oil contains acetic acid in the form of triacetin. In view of the extraordinarily high saponification and *Reichert-Meissl* values, which suggest the employment of this oil as a butter adulterant, a more exhaustive examination of the oil is required.

For the oil from *Evonymus verrucosa* cp. " Lesser known semidrying oils," table facing p. 238.

ANIS SEED OIL [1]

French—*Huile de graine d'anis.* German—*Anissamenol.*
Italian—*Olio di semi d' anice.*

This oil is obtained from the seeds of *Pimpinella anisum*, L., after the ethereal oil has been driven off. The seeds contain over 25 per cent of a fatty oil, which has a slight odour resembling that of henbane seed oil. The fatty acids yield on oxidation tetrahydroxystearic acid (sativic acid). The oil absorbs 2·7 per cent oxygen (determined by *Livache's* method) in three days. The specimen of oil examined by *Denjanow and Zypljankow* [1] had the acid value 6·3.

The following characteristics were determined :—

Oil—Specific gravity at 15° C.	.	0·924
Saponification value	.	178·3
Iodine value	.	105·3
Fatty acids—Solidifying point	.	0° C.
Iodine value	.	97·3 (?)

CROTON OIL

French—*Huile de croton.* German—*Crotonol.*
Italian—*Olio di crotontiglio.*

For tables of characteristics see p. 229.

Croton oil is obtained from the seeds of *Croton Tiglium*, L., a tree belonging to the *Euphorbiaceæ*, indigenous to the Malabar coast, and cultivated in Southern Asia and China. The seeds contain 53-56 per cent of oil.[2]

The oil has an amber-yellow, or orange, or brown colour according to its age, has a nauseous odour, a burning taste, and acts as a very powerful purgative. In pharmacy it is known as *Oleum crotonis*. According to *Kobert* [3] there are some kinds of croton oil in commerce

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[1] *Journ. Russ. Phys. Chem. Ges.*, 1905, 624.
[2] With regard to the occurrence of an enzyme in croton seeds cp. Scurti and Parozzani, *Gazz. Chim. Ital.*, 1907 (37), 486.
[3] *Chem. Zeit.*, 1887, 416.

that are miscible with *alcohol* in every proportion. This statement, however, only holds good of those oils that have been extracted from the seeds with alcohol. According to *Javillier* [1] oil obtained by expression or by extraction is only miscible with absolute alcohol if less than one volume be used; on mixing equal volumes of oil and absolute alcohol turbidity sets in, and with more alcohol complete separation into two layers takes place, whereas oil extracted with alcohol is soluble in absolute alcohol in every proportion.

The author examined three specimens of croton oil prepared for pharmaceutical purposes by reliable firms. One volume of oil was shaken up with three and a half volumes of absolute alcohol. After separation into two layers had taken place, the amount of oil dissolved by the alcohol was determined quantitatively. The alcohol had dissolved from the three samples—24·4 per cent, 25·5 per cent, and 53·4 per cent respectively. The respective specific gravities of the oils were 0·9428, 0·9418, 0·9375. Hence croton oil can no longer be classed together with castor oil, and the comparative great solubility of the oil in absolute alcohol must be ascribed to the large proportion of glycerides of volatile fatty acids. The larger the proportion of free fatty acids the greater will be the solubility of the oil in absolute alcohol. Thus the above-mentioned specimen, of which 24·4 per cent dissolved in alcohol, contained 7·9 per cent free fatty acids.

Croton oil further differs from castor oil by its solubility in petroleum ether in all proportions.

The chemical composition of croton oil differs so widely from that of all other oils that its recognition by means of the quantitative reactions is easy.

Croton oil is strongly dextro-rotatory (*Peter* [2]). It is stated to contain the following fatty acids :—Stearic, palmitic, myristic, lauric, valeric (isobutyl formic), butyric, acetic, formic, oleic, linolic,[3] and tiglic. On standing, croton oil deposits some " stearine." " Crotonoleic acid," said to constitute the purgative principle of the oil, and described as a non-volatile, unsaturated fatty acid, differing from oleic acid in that its barium salt was soluble in alcohol, is, according to *Dunstan and Bole*,[4] a resinous substance possessing a strong vesicating action.[5] Two samples examined by *Lewkowitsch* [6] had the true acetyl values 19·82 and 32·66 respectively. The proportion of unsaponifiable matter in several specimens amounted to 0·55 per cent.

Croton oil has weak drying powers ; it thickens somewhat on exposure to air. It yields no solid product in the elaïdin test.

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[1] *Journ. Pharm. Chim.* [6], 7, 521.

[2] Cp. also Raknsin, *Chem. Zeit.*, 1906, 143.

[3] Cp. Fokin, *Journ. Russ Phys.-Chem. Soc.*, 1907 (39), 607.

[4] *Journ. Soc. Chem Ind.*, 1895, 985.

[5] Its empirical formula is $C_{19}H_{18}O_4$; it is a hard, pale yellow, brittle resin, nearly insoluble in water, petroleum ether, and benzene, but easily soluble in alcohol, ether, and chloroform. On heating it softens gradually, and is quite fluid at 90° C. It has neither acid nor basic properties ; it is decomposed by boiling with alkalis, yielding a mixture of acids, and loses thereby its vesicating properties. This seems to point to this substance being a lactone or an anhydride.

[6] *Analyst*, 1899, 319

Physical and Chemical Characteristics of Croton Oil

	Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Reichert-Meissl Value		Refractive Index		
At °C	Per cent	Observer	°C	Observer	Milgrm. KOH	Observer	Per cent	Observer	c.c. norm KOH	Observer	°C	"de-grees"	Observer
15	0·9437	Duhère[3]	−7	Javillier	215	Lewko-witsch	106 6·109 1	Wijs	13 56	Lewko-witsch	oleo-refractometer 26	1·4781	Harvey
15·5	0·9373,[1] 0·9128[2]	Lewko-witsch			210 3	,,	101·7-102·6	Lewko-witsch	13·27	,,	°C	"de-grees"	Observer
100	0 8874	Duhère			215 6	Duhère	103 9-104 7	,,	12·1	Duhère	22	+·35	Duhère
					192 4-194 5	Javillier	104 4-105 5	Javillier			Butyro refractometer		
											°C	"de-grees"	Observer
											27	77·5	Duhère
											40	68	Lewko-witsch

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Acids. Unsaponifiable.		Solidifying Point		Neutralisation Value		Iodine Value	
	Per cent	Observer	°C	Observer	Milgrm. KOH	Observer	Per cent	Observer
	88·9	Lewko-witsch	18 6-19 7	Lewkowitsch	201	Benedikt	111 2-111 8	Duhère
	89 1	,,						

[1] 53·4 per cent soluble in alcohol.   [2] 24·4 per cent soluble in alcohol.   [3] *Journ. Soc. Chem. Ind.,* 1896, 1133; *Ann. Pharm.,* 1899 (5), **229.**
[4] Expressed oil ; acid value 27·3.   [5] Oil extracted with ether ; acid value 30·9.   [7] **Tier test.**
[6] A sample recently examined had the high iodine value of 122·3 (saponification value 210 2).

By hydrogenising a specimen of croton oil of the iodine value 99·8, *Paal and Roth's* method (see Vol. I. p. 59 ; in aqueous emulsion prepared with the aid of gum-arabic) a solid product was obtained, which conglutinated at 40° C., melted at 44°-48° C., and had the iodine value 4·8. On further treatment a solid fat melting at 49°-51° C. was obtained, which no longer absorbed iodine. The solubility in alcohol was somewhat less than that of the original oil, and the burning taste of croton oil was no longer noticeable. The specific physiological action of croton oil entirely disappeared in the hydrogenised fat.[1]

Owing to the slight similarity between croton oil and castor oil, adulteration of croton oil with castor oil has occurred. Castor oil in croton oil would increase the specific gravity, lower the iodine value, and raise the acetyl value considerably.

ZACHUN OIL, BETU OIL

French—*Huile de Zachun.* German—*Zachunol.*
Italian—*Olio di Zachune.*

This oil is obtained from the seeds of *Balanites ægyptiaca,* Delile, a tree found in northern tropical Africa, India, and Burmah.

The fruit, which is at first green, becomes red on ripening, and in its dry state somewhat resembles a date. It consists of a thin, brittle shell, enclosing a fleshy mass of gummy consistence which firmly adheres to the hard stone ; the latter furnishes the kernels. The kernels contain 49·64 per cent (*Suzzi* [2]) to 41·2 per cent (*Milliau* [3]) of fatty matter. A specimen of seeds collected from Ghinda in Erythrea (Italian African colony), gave the following characteristics (*Suzzi*) :—

Oil—

Specific gravity at 15°	.	.	.	.	0·9200
Solidifying point	.		.	.	–0° to 5° C.
Saponification value	.				194·1
Iodine value	.	.		.	105·0
Maumené test	.	.	.	.	75·5° C.

Fatty Acids—

Solidifying point	.		.	.	32°-30 5° C.
Melting point	.	.	.	.	34·5°-37° C.
Neutralisation number	.	.	.	.	200·0
Saponification value	.	.	.	.	201·6
Mean molecular weight	.	.	.	.	278·2

The samples contained 0·48 per cent free fatty acids (as oleic acid). The oil gave neither the *Halphen* nor the *Baudouin* reactions.

In the Egyptian Sudan the fruit is known as " Heglig " ; the oil

[1] *Berichte,* 1909, 1546.
[2] *I semi oleosi e gli Olii.* Published for the Milan Exhibition, 1906.
[3] *Agriculture pratique des Pays Chauds,* 1904, No. 16.

is highly prized by the natives. The following characteristics are given by the Gordon Memorial College : [1]—

Specific gravity at 100°/100° C.	. .	0·8819
Melting point . .	. .	8° C.
Saponification value	.	186·5
Iodine value .	. . .	99·2

A specimen of oil from Nigerian seeds,[2] yielding 58·7 per cent of oil, gave the following numbers :—

Oil —

Specific gravity at 15° C.	.	0·919
Saponification value		196·7
Iodine value .	.	92 5
Unsaponifiable matter .	.	0 6 per cent

Fatty Acids—

Insoluble acids + unsaponifiable	. .	95·2 per cent
Titer test		34·6° C.

In German East Africa the fruits are known as Mkonga fruits. Specimens from Morogoro yielded 8·8 per cent of seeds containing from 30·7 to 33 9 per cent of oil (*Morstatt* [3]). The oil obtained from the Mkonga seeds had the following characters (*Arnold* [4]):—

Specific gravity at 15° C.	0·9173
Saponification value	195·6
Iodine value .	77·2

A new oil-yielding tree, *Balanites Manghamii*, which is indigenous to Portuguese East Africa, produces nuts containing about 60 per cent of an oil said to resemble olive oil [5]

CURCAS OIL, PURGING NUT OIL, PHYSIC NUT OIL

French—*Huile de pignon d'Inde, de pulghère, de purghère, de médicinier.*
German—*Curcasol.* Italian—*Olio di curcas.*

For tables of characteristics see p. 233.

Curcas oil (*Oleum infernale*) is obtained from the seeds of *Jatropha Curcas*, L. (purging nut), by hot pressing. The plant is cultivated in tropical America and in all Portuguese colonies, chiefly in the Cape Verd islands.[6] In Réunion the plant is cultivated as a support of the vanilla plant. (The bark of the plant is covered with a wax which is most likely pure myricyl melissate (melissyl melissate), *J. Sack.*) The seeds consist of 66 per cent of kernels and 34 per cent of husks.

[1] 1908, 412.
[2] *Bull. Imp. Inst.*, 1908, 365.
[3] *Der Pflanzer*, 1910, 121.
[4] *Zeitschr. f. Unters. d. Nahrgs- u. Genussm.*, 1912, xxiii. 391.
[5] T. A. Sprague, *Kew Bull.*, 1913, iv. 131.
[6] Klein, *Zeitschr. f. angew. Chem.*, 1898, 1012.

The kernels yield on extraction with ether 52 per cent of oil, hence the oil in the whole seeds amounts to 34·3 per cent. The fresh oil has a pale colour, but becomes yellow with a reddish tint on exposure to the air. Its unpleasant odour is characteristic, and may serve to distinguish curcas oil from other oils; it is further characterised by its strong purgative properties, which are much more pronounced than those of castor oil.

The acid values of commercial samples were found by *Lewkowitsch* and *Archbutt* 8·5 and 0·7 respectively. *Klein* obtained values varying from 0·57 to 4·96. The proportion of unsaponifiable matter in the oil is 0·5 to 0·58 per cent (*Lewkowitsch; Klein*). The acetyl value found was 8·4 (*Lewkowitsch*) and 9·8 (*Archbutt*). 100 parts of absolute alcohol dissolve at 15·5° C. about 2·17 volumes of oil (*Archbutt*). The oil is insoluble in cold glacial acetic acid, but dissolves in the hot solvent.

On standing at a temperature of about 12° C. a small quantity of solid glycerides separate. According to *Klein* curcas oil yields about 10 per cent of solid fatty acids (melting at 57·5° C., and solidifying at 53·5° C.); the liquid fatty acids consist of about equal proportions of oleic and linolic acids as ascertained by the relative quantities of their oxidation products, viz. dihydroxystearic and tetrahydroxystearic acids. The existence of isocetic acid (Vol. I. Chap. III.), stated by *Bouis* to occur in curcas oil, is doubtful.

The oil is used in Portugal for soap-making, as an illuminant, and as a lubricating oil; it can, however, hardly be considered suitable for the last-named purpose, as the oil dries in about 24 hours (cotton seed oil drying under the same conditions in 18-20 hours, and good rape oil in 48 hours, *Archbutt*).

The seeds of *Jatropha oligandra*, Müll., yield about 31·5 per cent of a fatty oil of the specific gravity at 14° C. 0·910, having purging properties.

The seeds of *Jatropha multifida*, L., yield 28·5 per cent of a fatty oil of the specific gravity 0·918 at 25° C.

The seeds of *Jatropha mahafalensis* obtained from the south of Madagascar contain 60 per cent of a fatty oil of a yellowish colour and slight fluorescence. *H. Bimar* [1] ascertained the following characteristics :—

Oil—

Specific gravity at 15° C.	.	0·9213
Saponification value	.	194
Iodine value	.	114·8
Refractive index at 20° C.	.	1·4648

Fatty Acids—

Melting point	.	.	.	21° C.
Iodine value	.	.	.	110

[1] *Bull. Soc. Chim. de France*, 1911, 914; cp. also H. Jumelle and H. Perrier de la Bathie, *Les Matières grasses*, 1910, 2032.

Physical and Chemical Characteristics of Curcas Oil

Specific Gravity		Solidifying Point		Melting Point		Saponific. Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Refractive Index.	
At °C	Observer.	°C.	Observer.	°C.	Observer.	Mgrms KOH	Observer.	Per cent	Observer.	c.c. ¹⁄₁₀ norm KOH	Observer	°C.	Observer.	At 25° C.	Observer.
15	De Negri and Fabris	−8	Lewko-witsch	−4	Lewko-witsch	193·2	Lewko-witsch	109·9	De Negri and Fabris	0·55	Lewko-witsch	55·66·6	Archbutt	1·4681·1·487	Klein
,,	Arnaudon and Ubaldini							95·3	Lewko-witsch			68·8	Suzzi		
,,	Klein							104·9	Suzzi					Butyro-refractometer.	
15·5	Lewko-witsch													At °C	"De-grees	Observer.
														25	63	Lewko-witsch
														40	56·5	,,

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point		Melting Point		Iodine Value	
Per cent	Observer.	Titre Test	Observer	°C	Observer	Per cent	Observer
95·5	Lewkowitsch	28·6	Lewkowitsch	24·26	De Negri and Fabris	105·05	De Negri and Fabris

¹ *Journ. Soc. Chem. Ind.* 1898, 453   ² *Ibid.* 1898, 934   ³ *Chem. Revu* 1898, 211   ⁴ Oil from Erythrean seeds

The oil is stated to dry after exposure to a temperature of 50° C. in 26 hours.

The seeds of *Jatropha glandulifera* (a small evergreen tree common in India and also prevalent in the waste lands of tropical Africa) contain 21·3 per cent of a straw-coloured oil. The following characteristics were ascertained by *Menon* [1] in the author's laboratory :—

Oil—

Saponification value	194·5
Reichert-Meissl value . . .	4 [2]
Butyro-refractometer at 20° C.	76·5
,, ,, at 40° C. . .	68·5

Fatty Acids—

Melting point	35° C.
Iodine value	119·6
Neutralisation value . . .	187·3
Mean molecular weight . . .	299·4

BRAZIL NUT OIL

French—*Huile de noix de Brésil.* German—*Paranussol.*
Italian—*Olio di noci del Brasile.*

Brazil nut oil is obtained from the seeds of the Brazilian nut tree, *Bertholletia excelsa*, Humb. and Bonp., belonging to the *Myrtaceæ* (*Lecythiadaceæ*) (the " Para," or " Juvianus tree ") indigenous to the forests of the Orinoco and Amazon rivers, and now largely cultivated in tropical South America. The seeds bear the native name *kokobko* and are well known as " Brazil nuts " or " Para nuts." [3] They contain up to 73 per cent of the fatty oil, calculated to dry seeds [4] (the amount of water in the seeds being 7-8 per cent).

The oil has a pale yellow colour and is odourless ; its taste is similar to that of the nuts themselves.

On standing, even at the ordinary temperature, the oil deposits " stearine." A sample examined by *Niederstadt* [5] contained 16 per cent of free fatty acids. In South America Brazil nut oil is expressed for edible purposes.

The total export of Brazil nuts in 1908 amounted to 8200 tons, of which 4400 were exported to the United States, 3400 to the United Kingdom, and 300 to Germany.

[1] *Journ. Soc. Chem. Ind.*, 1910, 1430.
[2] This high value may be due to the oil having become rancid, as its acid value was 15·8.
[3] The Brazil nuts must not be confounded with the " sapucaia " nuts from *Lecythis Zabucajo*, yielding " Paradise nut oil." See below, p. 380.
[4] Greshoff, *Chem. Zeit.*, 1906, 856.   [5] *Berichte*, 1902, 144.

Physical and Chemical Characteristics of Brazil Nut Oil

Specific Gravity At 15° C.	Solidifying Point C	Saponification Value Mgrms. KOH.	Iodine Value Per cent	Maumené Test C	Refractive Index at 25°	Observer
0·9180	−4	193·4	106·22[1]	50-52	1·4643	De Negri and Fabris
0·9180	−2·5	202	98·3	...	...	Grimme[2]

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point C	Observer	Melting Point C	Observer	Neutralisation Value Mgrms. OH	Observer	Iodine Value Per cent	Observer	Refractive Index at 45 C	Observer	Insoluble Fatty Acids + Unsaponifiable Per cent	Observer
31·1-32·25[3]	Lewkowitsch	28-30	De Negri and Fabris	...	...	108	De Negri and Fabris	1·4528	Grimme		
		29·5	Grimme	196·7	Grimme	99·2	Grimme			96·82	Grimme

[1] The iodine value of Brazil nut oil extracted with solvents is given by De Negri and Fabris as 93 8-95·1. [2] *Chem. Revue*, 1910 265. [3] Titer test.

The nuts which have become mouldy in transit to Europe are expressed, and the oil thus recovered is used for soap-making, or as a substitute for inferior kinds of olive oil. An English patent of 1847 [1] claims the expression of Brazil nut oil for burning and lubricating purposes, the press cake to be used as cattle food and for manuring the land.

MUCUNA OIL [2]

French—*Huile de mucuna.*　German—*Mucunaol.*
Italian—*Olia di mucuna.*

This oil is obtained from the seeds of the different species of Mucuna, a plant belonging to the *Leguminosæ*, viz. *M. urens, M. pruriens,* De C.,[3] *M. cylindro-sperma, M. monosperma.*

The oil characterised in the following lines was obtained from the seeds of the " cow-itch " bean, *Mucuna capitata,* De C, occurring in the Dutch Indies (described in Rumphius' *Herbarium Amboinensis* as *Cacara nigra*). The freshly ground seeds yielded to petroleum ether 2·08 per cent of an oil having the acid value 6·7. The oil extracted from ground seeds which had stood for about two months showed a higher specific gravity, higher acid value, higher saponification value, and lower iodine value.

Amongst the solid fatty acids palmitic acid and stearic acid were identified. The acetyl value was determined by *Benedikt and Ulzer's* method, but in view of the strictures passed by the author on this method (Vol. I. Chap. VIII), the number is not recorded here.

Physical and Chemical Characteristics of Mucuna Oil

Specific Gravity at 100 (water 15 =1)	Solidifying Point ° C	Melting Point ° C	Saponification Value Mgrms KOH	Iodine Value Per Cent	Reichert-Meissl Value c c $\frac{1}{10}$ KOH	Refractive Index Butyro-refractometer " Degrees " at 25° C
0·865	3·5	16	178 22	104	0·77	66 2

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Melting Point.	Neutralisation Value.	Iodine Value.
37°	195·6	112·9

[1] J. B. Wilks, Engl. patent 1774, 1847.
[2] W P. H. Van der Driessen Mareeuw, *Pharm. Weekblad,* 1906, No. 9 ; 1909 (46), 881.
[3] This species appears to be identical with *Mucuna prurita,* Hook., the leaves of which are used for dyeing black.

SORGHUM OIL

French—*Huile de sorgho.*   German—*Sorghumöl.*
Italian—*Olio di sorgo.*

Sorghum oil obtained from the dried seeds of *Sorghum cernuum,*
Host., which is largely cultivated in Turkestan, is characterised by a
peculiar odour ; it represents a yellow, vaseline-like mass which dries
slowly.

Physical and Chemical Characteristics of Sorghum Oil

Specific Gravity at 15° C	Melting Point ° C.	Saponification Value	Iodine Value.	Reichert Meissl Value
0 9282	39·40	172·1	98 89	2·1

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable	Melting Point C	Iodine Value
96 1	43·44	101·63
		Iodine Value of the Liquid Fatty Acids
		148 08

The specimen examined by *Andrejew* [1] had an acetyl value of 6·85.
The amount of lecithin calculated from the phosphorus in the ash was
0·23 per cent.   According to *Andrejew*, the mixed fatty acids of the oil
consist chiefly of erucic acid, and small quantities of oleic, nemoleic,
and linolic acids.   These statements stand in need of confirmation.

This oil must not be confounded with the oil from *Sorghum vulgare.* [2]

COUMOU OIL, [3] BATAVA OIL [4]

French—*Huile de coumou.*   German—*Comuol.*
Italian—*Olio di coumou.*

Coumou oil is obtained from the kernels of the palm trees : *Œno-
carpus batava,* Mart., *Œ. bacaba,* Mart., which frequently occur in

[1] *Chem. Zeit. Rep.*, 1903, 283.   [2] *Chem. Revue*, 1904, 106.
[3] Bassière, *Journ. Pharm. Chim.*, 1903, 323.
[4] Patava oil appears to be a corruption of batava oil.

Fatty Oils from Plants of the Order Umbelliferæ [1]

		Oil							Fatty Acids				
German	Source	Specific Gravity	Solidifying Point	Refractive Index	Saponification Value	Iodine Value (Wijs)	Fatty Acids	Unsaponifiable Matter	Melting Point	Solidifying Point	Neutralisation Value	Mean Molecular Weight	Iodine Value (Wijs)
			°C				per cent	per cent	°C	°C			
ümmelöl	Carum Carvi, L.	0·9268 (15°)	-5°	1·4710 (35°)	178·9	128·5	04·06	2·74	-7°	8° to -10°	182·8	307·2	124·6
eteralienöl	Petroselinum sativum, Hoffm.	0·9245 (15°)	-14°	1·4773 (55°)	176·5	109·5	91·67	2·18	-7° to -8°	-10°	180·1	316·0	93·4
ellericol	Apium graveolens, L.	0·9236 (15°)	-19°	1·4783 (55°)	178·1	94·8	89·00	0·79	-2°	4° to -5°	177·2	316·0	93·4
usol	Pimpinella Anisum, L.	0·9232 (15°)	-8°	1·4738 (16°)	178·4	108·6	92·62	0·96	1-2° to -8°	6°	179·0	313·7	110·0
'enchelöl	Foeniculum officinale, All.	0·9304 (15°)	-8°	1·4705 (55°)	181·2	99·0	89·82	3·68	1-1° to -2°	0°	180·5	311·1	98·9
illöl	Anethum graveolens, L.	0·9282 (25°)	-7°	1·4795 (35°)	176·0	119·6	92·56	1·14	5°	1°-2°	179·0	313·7	102·7
kohrenöl	Daucus carota, L.	0·9296 (15°)	-4°	1·4723 (30°)	179·4	105·1	92·0	1·53	-1° to -2°	5°	181·6	309·3	90·1
ömisch Kümmelöl	Cuminum Cyminum, L.	0·9256 (15°)	-8°	1·4729 (30°)	179·3	91·8	91·53	2·06	-1°	4°	183·2	307·3	115·7
tartenkerbelöl	Anthriscus cerefolium, Hoffm.	0·9285 (15°)	-9°	1·4672 (35°)	183·1	110·2	91·32	1·45	4° to 6°	1°	179·6	312·6	98·6
orlandornöl	Coriandrum sativum, L.	0·9284 (15°)	-4°	1·4704 (30°)	182·0	99·8	91·14	2·20	3° „ 4°	3°	178·0	315·5	102·2
jovanol	Ptychotis ajowan, D.C.	0·9267 (15°)	5°	1·4710 (55)	176·8	108·8	92·56	1·13	4° „ 5°	3°	178·0	315·5	102·2

1 C. Grimme, Pharm. Zentralh., 1911, 661.

Fatty Oils from Plants of the Order Papilionaceæ [1]

		Oil								Fatty Acids			
German	Source	Yield	Specific Gravity	Solidifying Point	Saponification Value	Iodine Value	Refractive Index	Fatty Acids	Unsaponifiable Matter	Melting Point	Solidifying Point	Neutralisation Value	Mean Molecular Weight
		per cent		°C				per cent	per cent	°C	°C		
erbsenöl	Cicer arietinum, L.	5·1	0·9184 (15°)	-15	182·6	115·5	1·4717 (30°)	92·62	1·08	18 to 21	15 to 16	189·4	296·5
öl	Pisum sativum, L.	1·0	0·9193 (15°)	-12	184·5	106·0	1·4766 (35°)	92·68	1·32	26 „ 27	24 „ 25	185·5	304·1
nnenöl	Vicia Faba, L. var. major	1·07	0·9175 (15°)	-11	184·7	99·6	1·4758 (30°)	91·81	1·94	25 „ 26	22 „ 23	183·3	306·4
öl	Vicia sativa, L.	1·05	0·9204 (20°)	8	180·5	107·2	1·4705 (30°)	90·89	2·20	30 „ 32	26 „ 28	180·8	316·6
lckenöl	Vicia sepium, L.	1·4	0·9206 (15°)	-8	183·1	111·0	1·4748 (40°)	91·81	2·04	33 „ 34	30 „ 31	185·0	302·1
öl	Lens esculenta, Moench.	0·83	0·9211 (25°)	6	182·4	100·4	1·4706 (40°)	92·06	1·78	25 „ 26	22 „ 23	182·0	308·6
ohnenöl	Cytisus sessilis, Spreng.	1·22	0·9198 (25°)	2	188·2	102·7	1·4653 (35°)	91·31	2·33	29 „ 31	24 „ 25	185·7	302·5
bohnenöl	Phaseolus Mungo, L.	1·85	0·9208 (25°)	9+0	187·5	111·3	1·4640 (35°)	87·51	5·85	32 „ 33	27 „ 28	180·5	311·0
öl	Phaseolus vulgaris albus, Haberle	1·32	0·9179 (15°)	4	180·2	135·7	1·4789 (40°)	91·95	1·69	14 „ 15	10	187·0	300·3
ohnenöl	Phaseolus coccineus, Lam.	1·83	0·9198 (15°)	-12	189·6	111·2	1·4760 (40°)	92·32	0·98	29 „ 31	13	188·2	298·4
ohnenöl	Phaseolus lunatus, L.	1·0	0·9212 (25°)	1	189·3	99·8	1·4772 (40°)	92·23	1·11	26 „ 27	26	182·8	307·2
unschonen Bohne	Phaseolus inamoenus, L.	1·26	0·9206 (25°)	-2	188·7	118·9	1·4646 (45°)	92·23	1·54	35 „ 36	33	180·0	312·6
ohnenöl	Dolichos Lablab, L.	1·42	0·9192 (25°)	2	187·5	94·4	1·4716 (45°)	91·86	1·60	35 „ 36	32	189·4	296·5
ohnenöl	Vigna catjang, Endl.	1·28	0·9228 (25°)	-2	185·6	100·8	1·4672 (40°)	93·79	1·29	32 „ 34	20	189·0	297·1
rbohnenöl	Canavalia ensiformis, D.C.	2·81	0·9160 (15°)	-7	188·5	86·1	1·4685 (45°)	92·78	1·29	26 „ 27	12	185·1	303·4
renöl	Voandzeia subterranea, Thou.	6·24	0·9176 (15°)	2	184·1	112·0	1·4626 (40°)	92·30	1·38				

1 C. Grimme, Pharm. Zentralh., 1911, 1141.

Face

Fatty Acids.

Oil from	Solidifying Point.	Neutralisation Value	Mean Molecular Weight.	Iodine Value (Wijs).	Refractive Index. at 35°.
	°C				
Caraway seed	8° to -10°	182 8	307 2	124 6	1·4679
Parsley seed	-10°	180 1	311 8	108 2	1·4679
Celery seed	-4° to -5°	177 2	316 9	93 4	1 4778
Anise seed	0°	179 0	313 7	110 0	1 4704
Fennel seed	0°	180 5	311 1	98 8	1 4710
Dill seed	1°-2°	181 0	310 3	114 2	1 4760
Carrot seed	5°	179 0	313 7	102 7	1·4625
Cumin seed	4°	181 6	309 3	90 1	1 4748
Chervil seed	2°	183 2	307 3	115 7	1 4580
Coriander	1°	179 6	312 6	98 6	1·4593
Ajowan seed	3°	178 0	315 5	109 2	1 4650

Fatty Acids

Oil from	ig	Solidifying Point.	Neutralisation Value	Mean Molecular Weight	Iodine Value (Wijs)	Refractive Index
		°C.				
Chick pea	1	15 to 16	189 4	296 5	120 3	1 4587 (40)
Common pea	7	24 ,, 25	183·5	306 1	108 4	1 4659 (35°)
Broad bean	6	22 ,, 23	183 3	306·4	102 0	1 4679 (35°)
Vetch	2	26 ,, 28	180 8	310·6	105 8	1 4704 (35°)
Lentil	4	30 ,, 31	185 9	302·1	111·9	1·4704 (35°)
Pigeon-pea	6	22 ,, 23	182 0	308 6	103 0	1 4698 (40°)
	1	24 ,, 25	185·7	302 5	104 0	1 4691 (35°)
Minogo bean	3	27 ,, 28	185 8	302 4	114·2	1 4723 (40°)
Haberle haricot bean	3	19	180 5	311 0	136·0	1 4679 (40°)
Scarlet runner	5	13	187 0	300 3	143 6	1 4653 (40°)
Moon-bean	1	26	188 2	298·4	101·6	1 4704 (45°)
	7	23	182·8	307 2	121·7	1 4640 (44°)
	6	33	180 0	312 0	97 0	1 4633 (45°)
	6	32	189 4	296 5	99 4	1 4620 (40°)
Fetich bean	4	29	180 0	297 1	92 3	1 4593 (45°)
Thon	7	22	185 1	303 4	112 8	1 4566 (45°)

Name of Oil	French	German	Italian	Source	Native Country	Oil						Fatty Acids						Acid Value	Observer
						Yield per cent	Specific Gravity	Saponification Value	Reflux Value	Iodine Metal Value	Refractive Index	Neutralisation Value of Fatty Acids	Insoluble Acids + Unsaponifiable	Solidifying Point of Fatty Acids °C	Melting Point of Fatty Acids °C	Iodine Value of Insoluble Fatty Acids	Refractive Index of Fatty Acids		
Laburnum seed oil	Huile de cytise	Goldregenmandl	Olio di cilias	Cytisus Laburnum, L.	..	..	..	182·4	186·7	..	71·1° at 25° C.	..	..	..	..	..	..	..	Diobichne [1]
Apple seed	Huile de pommier	Apfelmandl	Olio di mela, L.	Pirus malus, L.	..	20	0·9119	198	143	..	1·4727 at 25° C.	286·3	97·0	..	..	..	..	65·66 (?)	1·47087	67·4	R. Meyer [2]
Pear seed	Huile de poirier	Birnenmandl	Olio di pera	Pirus communes, L.	..	19	0·9177	118 (?)	121	..	1·47178 at 25° C.	198	91·0	28	25	102·104	1·47273	30	"
Ash seed	Huile de frêne	Eschenmandl	Fructus excelsior	Europe	6·7	0·9166	168·3	129·6	1·96	..	181·7	..	28·6	..	..	123·6	..	..	W. Koch [3]
Hura seed	?	?	?	Gynocardia periaptifolia	East India	..	..	184·6	110·6	..	..	..	..	..	..	..	..	8·4	D. Hooper [4]
Small Fennel	Huile de nigelle	Schwarz Kummel	Olio di cinninella	Nigella sativa, L.	"	23·74	0·9288 (15° C.)	198·5	110	..	56·5° at 40° C.	197·9	..	−10° to −16°	..	..	..	..	Crossley and Le Sueur [5]
Indian Laurel	Huile de laurier Indien	Indisches Lorbeerül	Olio di lauro Indico	Laurus nobilis	"	32	0·925 at 15° C.	178 (?)	119·6	..	..	16° · 19° C.	24°·28° C.	..	..	..	De Nigri and Fabris [6]
Tobacco seed	Huile de tabac	Tabaksmandl	Olio di tabacco	Nicotiana Tabacum, L.	"	28	0·9223 at 15° C.	190	119·6	..	..	94·78	..	..	..	..	Ampola and Scurti [7]
?	?	?	?	Euphorbia obtusta	Mexico	..	..	208·4	110·4	..	..	93·0	25·27° (?)	..	..	..	2·4	R. Okuda [8]
?	?	?	?	Euphorbia pagona, Karisch	German South West Africa	38·6 30·26	0·9072 at 15° C. 0·925	196·0 220·(?)	105 104	2·06	71·5° at 15° C. 1·4710 at 21° C.	.. 280 (?)	95·90 96·9	95·58 98	35·97 40	74 (?)	1·47840 at 31° C.	38·1	W. Leua [9] R. Meyer [10]
Orange seed	Huile d'oranger	Orangenmandl	Olio d'arancia	Citrus aurantium, Risso	French Congo	11·3	0·907 (?)	187·6	101	..	..	96·9	..	14	..	..	..	R. Henkel [11]
Guaco seed oil	Huile de cusso	?	?	Manniophyton fulvum	Brazil	..	..	188·47	98·3	..	..	..	..	..	..	..	..	Niederstadt [12]
?	?	?	?	Jatrophia princeps, Velus		..	0·910 (15° C.)	192·0	98·4	..	..	..	86	..	..	..	..	Imp. Inst. [13]
?	?	?	?	Calodendron capense	Brazil	..	..	195·68	80·0	..	..	..	..	..	..	..	..	
?	?	?	?	Sapucaia flora, Velus	North India	..	..	190·20	86·0	0·10	..	96·2	..	..	..	..	14·6	D. Hooper [14]
?	?	?	?	Ocklingtonum prungunum		..	..	..	..	..	..	..	..	..	..	..	..	
Chinese vhoautu seed oil	Huile d'anis étoilé	Chinesisches staranismandl	Nisaex carum, Hook. fil.	China	13	0·9284 at 15° C.	193·6	98·1	1·4	..	259·2	65·2 (?)	..	..	127·8	..	J. Bolle [15]
Japanese staranis seed oil	Huile d'anis japonais	Japanisches staranismandl	Illicum religiosum, Sieb.	Japan	8	0·9245 at 15° C.	193·4	90·8	1·5	..	280·7	95·0	..	..	108·7	..	"
Barley seed	Huile d'orge	Gerstenmandl	Olio d'orzo	Hordeum vulgare, L.		..	0·9244	199	90	..	..	289	88	..	..	69·8 (?)	1·4748 at 36° C.	25	R. Meyer [16]
Brazln nut, Niekar seed	Huile de palmchikir boulou (oil de chat)	Broadmandl	Casalpmia Bonduella, Roxb.	Brazil	..	..	..	89·9	..	..	..	..	..	..	..	..	Niederstadt [17]
Coriander seed	Huile de coriandre	Coriandermandl	Olio di coriandro	Coriandrum sativum, L.		5	0·9116	68 (?)	88·5	..	1·4698 at 22° C.	155 (?)	98 (?)	..	..	86·7	1·47529 at 28° C.	16·4	R. Meyer [18]
Tamarind seed	Huile de Galden des Indes	Tamarindenmandl	Olio di tamarindo	Tamarindus indica, L.	Tropical Asia	4·5	..	188	87·1	..	..	94·0	..	48	..	..	..	D. Hooper [19]
Sorn	?	Farrnkrautol		Asplodum filix mas [20] L.		..	..	..	86·4	..	..	..	..	..	..	..	..	Halz [21]
Paprika	Huile de pointe de Guinée	Paprikaol	Olio di paprica	Capsicum annuum, L.		20	0·92568	270·(?)	86·5	..	1·4729 at 21° C.	..	92	27	38	66·(?)	..	52	R. Meyer [22]
Bean oil	Huile de fève	Bohnenmandl	Olio di fava	Faba faba, L.		..	0·9270 at 16° C.	196	82	..	..	88·3 (?)	..	31	113·(?)	1·47889 at 30° C.	116	"
Rye seed	Huile de seigle	Roggenmandl	Olio di segale	Secale cereale, L.		..	0·9331	196	81·88	..	1·47985 at 25° C.	109	88·9	34	28	113	1·4716 at 30° C.	46·6	"
?	Huile de kampuncle	?	?	Inctium densucsum [23]		26	..	..	..	..	..	..	..	..	..	147·9	..	Fahn [24]
?	?	?	?	Gebopua lalanus [25]		49·4	0·922 at 20° C.	..	..	..	..	..	..	..	..	142·0	..	"
?	Huile d'agripaume ou cardiaque	?	?	Leonurus cardiaca [26]		25	0·928 at 20° C.	..	..	..	..	..	..	..	..	138·7	..	"
Huckistraw oil	Huile de fléal à petite feuille	Lindmandl	Olio di tiglio	Tilia parvifolia, [27] T. cordata, Mill.		58·6 [28]	0·928 at 20° C.	194·6	123·6	..	..	187·0	93·1	9·88	17·32	138·3	..	"
Syphnllacene oil	Huile de kanin verruquena	Sybnllsbmandl	Olio di tsnaghia	Evonymus verrucusus [29] [30]		43·84	0·928 at 20° C.	..	..	4	..	188·6	..	33·33	..	110·6	..	"
Larkspur oil	Huile de larphindle élevée	Rittersporn ol		Delphinium elatus [31] [32]		68·6	0·925 at 20° C.	..	..	..	72·7 [33]	181·8	..	..	..	108·2	506 in Batyo-nitrobenzene	"

Footnotes:

[1] Aeta f Unters. Nahrip- u Genuss., 1883, xxv 129. The seeds carry poisonous

[2] Rosen Bollye refractometer

[3] Chem Zeit, 1905, 936. The figures quoted stand in need of confirmation.

[4] Chem Zeit, 1911, 673

[5] Jour Soc Indiau Nature, 1906-9, p 19

[6] J une siour a p R ott Milan Richtlinien, 1906

[7] Cp 4th Edition, Vol II, p 234

[8] Chem Zeit. Rep, 1906, 149

[9] Gaze Chim Ital, 1894 (24), 513. The fatty acids are stated to contain 15 per cent oleic acid, 45 per cent linolic acid, 23 per cent palmitic acid, and small quantities of stearic acid

[20] Apotheker Zeit., 1910, 1014. The statement that the oil contains oleic, linolic, and linolenic acids, and also a hydroxy acid must be accepted with reserve. The figure given by Okuda for the titer test has been quoted.

[21] Ark, u. d. Pharm. Inst, Unav Berlin, 1929 (9), 237. The above figures refer to expressed oil.

[22] This plant belongs to the Euphorbiaceae

[23] La Natiers prines, 1911, 2155.

[24] Bull. Imp Inst, 1909, 934. Unsaponifiable matter, 11 per cent.

[25] This bean has been suggested as a source of "silkcotton" (the "Kapok").

[26] The Agricultura Ledger, 1906, No. 9, Calcutta.

[27] Zeit. f Unters. d. Nahrp- u. Genussm., 1912, xxiv, 511. The fatty acids are

stated to consist of : Oleic acid, 46 per cent, linolic acid, 28·5 per cent, palmitic acid, 24·5 per cent, stearic acid, 1·0 per cent.

[28] The fatty acids are stated by Bolle to consist of : Oleic acid, 30·5 per cent; linolic acid, 7·6 per cent; palmitic acid, 21·5 per cent; stearic acid, 5·5 per cent.

[29] Termed made are universally eaten by the poorer classes in India during times of famine.

[30] The high melting point is due to the presence of an acid melting at 74° C (probably arachidic acid).

[31] The fatty oil from Asplidium phalenum is stated by Fahn (Arch. d. Pharm., 1904, 17) to consist chiefly of oleic. About 4 per cent of linolic acid were shown to be present amongst the fatty acids.

[20] Agricultural Ledger, 1907, No. 1, p 18

[28] The oil contains the glycerides of palmitic, cerotic, and oleic acids, the saturated acids forming about 4·5 per cent of the total fatty acids (Jordi d Pharm, 1904, 635).

[29] Amongst the liquid fatty acids linolic acid is present, linolenic acid is absent.

[27] Chem Zeine, 1904, 72.

[28] Other kinds of linden seeds are stated to contain 58 per cent of oil.

[29] Specific gravity of the mixed fatty acids, 0·912

[30] Specific gravity of the mixed fatty acids, 0·903 at 20° C

[31] Amongst the liquid fatty acids linolic and linolenic acids are present.

(β) The Rape Oil Group

All the members of this group are obtained from seeds of plants belonging to the *Cruciferæ*.

Their drying powers are not of a pronounced character; the elaïdin obtained from them is a buttery mass.

The most characteristic property of the oil of this group is that their saponification values are lower than those of any other vegetable oil, owing to the presence of erucic acid in these oils. Arachidic acid also appears to form a normal constituent; this acid has been found in a large number of rape oils, as also in a specimen of mustard oil.

The opinion held for a long time that these oils contain sulphur has been shown to be erroneous; all "cold-drawn" rape oils are free from sulphur, and absence of that element in an oil does not, therefore, prove absence of rape oil.

This opinion is due to the fact that cruciferous seeds (especially mustard seeds) contain potassium myronate (sinigrin) and an enzyme (myrosin) which in the presence of moisture produces glucose and amongst other products allyl isothiocyanate. Hence frequently cakes kept under unsuitable conditions give rise to the development of (ethereal) mustard oil.[1]

Presence of sulphur in rape oils may, however, point to a rape oil which has been expressed at a high temperature or extracted with carbon bisulphide.

I describe under this group the following oils : Garden cress oil, ravison oil, rape oil, black mustard oil, white mustard oil, radish seed oil, jamba oil.

GARDEN CRESS OIL

French—*Huile de cresson alénois.*   German—*Gartenkressensamenol.*
Italian—*Olio di crescione.*

For tables of characteristics see p. 240.

Garden cress oil is obtained from the seeds of the garden cress, *Lepidium sativum*, L., containing from 23 to 25 per cent of oil.

The high iodine value of this oil, and especially its exceptionally high thermal reaction, place it nearer to the two oils from cruciferous plants described already, viz. cameline oil and garden rocket oil (drying oil), than to the other oils of the rape oil group. Garden cress oil ranks, therefore, among the slowly drying oils.

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[1] For the determination of ethereal mustard seed oil cp. p. 263, and C. Brioux, *Ann. Chim. Analyt.*, 1912, 3.

Physical and Chemical Characteristics of Garden Cress Oil

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Maumené Test		Refractive Index	Refractive Index		Viscosity	
											Butyro-refractometer "Degrees."			
At °C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.		At 40° C.	Observer.	Seconds at 70° F.	Observer.
15 (water at 15=1)	De Negri and Fabris	−6 to −15	Suzzi¹	178	De Negri and Fabris	108-108·8	De Negri and Fabris	92-95	De Negri and Fabris					
15	0·920 Grimme	−15 to −16	Grimme	183·7	Grimme	133·5	Grimme			1·4718 at 20° C. Grimme	60·5	Crossley and Le Sueur²	321·6	Crossley and Le Sueur
15·5 (water at 15·5=1)	0·9238 0·9210- 0·9221 Crossley and Le Sueur²			181·5- 183·1	Crossley and Le Sueur²	101·72- 118·4	Crossley and Le Sueur²							
20	0·9212³ 0·9221⁴ Wijs			186·4³ 185·6⁴	Wijs	133·4³ 139·1⁴ 128·5	Wijs ,, Suzzi¹	89·5	Suzzi¹					

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Solidifying Point		Melting Point		Iodine Value		Neutralisation Value		Mean Molecular Weight		Refractive Index	
Per cent.	Observer.	°C	Observer.	°C.	Observer	Per cent.	Observer.	Mgrms KOH.	Observer.		Observer.	At 25° C.	Observer.
95·57	Crossley and Le Sueur			16-18	De Negri and Fabris	111·40	De Negri and Fabris	193·63 193·44	Wijs Suzzi¹	291·4 290·4	Wijs ,,		
				20-21·4	Wijs	137·73 144·94	Wijs	186·7	Suzzi¹				
94·98	Grimme⁵	22·23	Grimme	25-26	Grimme	138·1	Grimme	191·1	Grimme	293·2	Grimme	1·4650	Grimme

¹ Oil from Erythraean seeds. ² Two oils from Bengal and the Punjab respectively. Journ. Soc. Chem. Ind., 1898, 991   ³ Expressed oil.
⁴ Extracted oil.   ⁵ Chem. Revue, 1912, 102. Unsaponifiable matter, 1·23 per cent.

On saponifying the oil, its peculiar odour disappears, and an unpleasant fish-like smell is developed, more strongly in the case of extracted than of pressed oil. On liberating the fatty acids, the original odour reverts to some extent.

In East India garden cress oil is used as an edible oil.

RAVISON OIL

French—*Huile de ravison.*   German—*Ravisonol.*
Italian—*Olio di ravizzione.*

For tables of characteristics see p. 242.

The oil from Black Sea rape seed, a kind of wild *Brassica campestris* (cp. " Rape Oil," p. 243), is known in commerce as Black Sea rape oil or ravison oil.   The seed contains 33-40 per cent of oil.

Ravison oil, like rape oil, contains small amounts of arachidic acid. Specimens of ravison oil examined by *Archbutt and Deeley* [1] yielded from 1·45 to 1·66 per cent of unsaponifiable matter. A sample examined in my laboratory prepared from ravison seed contained 1·83 per cent.

Ravison oil has a higher iodine value than rape oil and exhibits stronger drying properties.   It is therefore not so suitable for lubricating purposes as rape oil, and its admixture with (or substitution for) rape oil must be looked upon as adulteration.   Since ravison oil is mostly extracted by means of solvents, traces of the latter are left in the oil. They are most readily detected by taking the flash point of the oil. A commercial oil examined by the author had the flash point 396° C. (in *Gray's* tester, Vol. III. Chapter XV.).

[1] *Lubricants and Lubrication*, p. 106.

Physical and Chemical Characteristics of Ravison Oil

Specific Gravity			Solidifying Point		Saponification Value		Iodine Value		Maumené Test.		Refractive Index. Oleo-refractometer.		Viscosity (Redwood's Viscosimeter).	
°C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C	Observer.	"Degrees."	Observer.		Observer.
15	0·9175-0·921	Cloez	-8	Jean	174	Jean	105	Jean	45[1]	Jean	+25 +18[2]	Jean	about 6-13% lower than refined Rape Oil 334-352 seconds at 70° F.	Archbutt and Deeley
15·5	0·9183-0·9217	Archbutt and Deeley			177·9-179·3	Archbutt and Deeley	108·9-121·7	Archbutt and Deeley	65·8-76	Archbutt and Deeley	+16 to +20	Pearmain	385 at 70° F.	,,
,,	0·9146-0·9179	Lewkowitsch			172·9-177·2	Lewkowitsch	101·4	Tortelli and Ruggeri					95 at 140° F.	,,
,,	0·9204	,,			178·5	,,	115·2-117·4 120·4[3]	Lewkowitsch ,,					334 at 70° F.	Lewkowitsch

Butyro-refractometer.

At °C.	Degrees.	Observer.
20	74	Lewkowitsch
25	71·5	

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity.			Iodine Value.		
°C.		Observer.	Per cent.		Observer.
100	0·8802	Archbutt and Deeley	126·1[3]		Archbutt and Deeley

Iodine Value of Liquid Fatty Acids

194·2		Tortelli and Ruggeri

1 By Jean's thermometer.   2 Italian ravison.   3 Iodine value of the oil 121·7.

RAPE OIL [COLZA OIL]

French—*Huile de colza.* German—*Rüböl.*
Italian—*Olio de colza.*

For tables of characteristics see pp. 245–248.

Tho different kinds of commercial rape oil are obtained from the seeds of *Brassica campestris* and several largely cultivated varieties of this species belonging to the natural order *Cruciferæ.* The oils from these plants are indiscriminately termed rape oil or colza oil, especially in this country ; on the Continent, however, two different kinds of oil are understood under the last two names. According to the variety of the plant from which the seed is derived, the following oils may be broadly differentiated :—

1. Rape oil (French—*Huile de navette* ; German—*Rapsöl, Repsol*) from the seeds of *Brassica campestris,* var. *Napus,* L.

2. [Rubsen oil] French—*Huile de rabette* ; German—*Rübol, Rübsenol* ; from the seeds of *Brassica campestris,* var. *Rapa,* L.

Both Brassica species furnish several, by no means sharply distinguished, varieties, which are again divided, according to the season of the year, into several races. Thus *Brassica Napus oleifera biennis,* Roxb. (=*B. Napus B. oleifera,* D.C.=*B. N. oleifera hiemalis,* Doll.) yields the *winter variety* (Winterraps, Winterkohlraps, Setzölsamen, Lewat, Kohlraps, Kohlsaat or *Colza*) ; and the annual form, *Brassica Napus oleifera præcox,* Roxb. (=*B. N. annua,* Koch=*B. N. oleifera annua,* Metzg.), the summer variety (Sommerreps, Sommerkohlrepps, Sommerkohlsaat, Summercolza).

Brassica Rapa (=*B. asperifolia,* Lam.=*B. campestris,* L.) also is grown as a winter seed (*Br. Rapa oleifera,* D.C.=*B. R. oleifera biennis,* Metzg.=*B. campestris, B. oleifera,* D.C.=*Br. R. oleifera hiemalis,* Martens) termed in Germany Winterrübsen, Winterölrübe, Wintersaat, Rübsaat ; and, as a summer seed, *Brassica Rapa oleifera annua,* Metzg. (=*Br. campestris,* Koch=*Br. campestris,* L.=*Br. præcox,* Kitaibel=*Br. R. oleifera*).

Although the winter and summer varieties of rape oil differ in consistence, the summer oil being thinner and solidifying at a lower temperature, it is impossible to distinguish further the last-mentioned varieties by their chemical or physical characteristics. Moreover, as in the trade all three varieties are indiscriminately sold (at any rate in this country) as *rape oil* or *colza oil,* I comprise within the two tables of the physical and chemical characteristics of the oil and its mixed fatty acids all the data that have been furnished by the several observers who examined the commercial rape oils. It is very desirable, however, that full particulars as to variety and source be given when characteristics of rape oils are published.

C. Grimme [1] has undertaken an exhaustive inquiry of this kind

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[1] *Pharm. Zentralh.,* 1912 (27), 733.

into the varieties of *Brassica oleracea*, L.; *Brassica Rapa*, L.; and *Brassica Napus*, L.; and has given the characteristics of the oils and fatty acids derived from (1) the following ten varieties of *Brassica oleracea*, L.:— *B. o. acephala vulgaris*, D.C.; *B. o. a. quercifolia*, D.C.; *B. o. a. crispa*, D.C.; *B. o. gemmifera*, D.C.; *B. o. sabauda*, L.; *B. o. capitata alba*, L.; *B. o. capitata rubra*, L.; *B. o. gongylides*, L.; *B. o. botrytis*, L.; *B. o. asparagoides*, D.C.; (2) the following four varieties of *Brassica Rapa*, L.:—*Brassica Rapa oleifera annua*, Koch; *B. R. o. hiemalis*, Martens; *B. R. rapifera*, Metzger; *B. R. teltoviensis*, Alefeld; (3) the following five varieties of *Brassica Napus*, L.:—*B. N. oleifera annua*, Koch; *B. N. o. hiemalis*, Doell; *B. N. o.*, D.C., *flore alba*; *B. N. rapifera*, Metzger; *B. N. rapifera*, var. Metzger.

For the details of this laborious research the reader must be referred to the original paper. It may suffice here to collate the *maxima* and *minima* for the oils from the *Brassica species* :—

	Brassica oleracea 10 Varieties.	Brassica Rapa 4 Varieties.	Brassica Napus 5 Varieties.
Oil—			
Specific gravity at 15° C.	0·9198–0·9226	0·9170–0·9200	0·9172–0·9210
Solidifying point, ° C.	– 4 to – 9	– 6 to – 10	– 5 to – 12
Saponification value	174·4–180·3	174·7–178·9	171·3–180·1
Iodine value	93·6–101·9	96·4–100·0	95·3–104·6
Refractive index at 20° C.	1·4723–1·4739	1·4723–1·4728	1·4710–1·4726
Fatty Acids—			
Fatty acids, per cent.	93·89–94·53	94·10–94·28	94·14–94·80
Unsaponifiable matter, per cent	0·72–1·42	0·92–1·04	0·83–1·12
Solidifying point, ° C.	6–19	9–15	6–15
Melting point, ° C.	11–21	13–17	8–19
Neutralisation value	177·0–181·8	177·2–183·5	175·4–181·3
Mean molecular weight	307·2–318·0	306·0–317·0	309·8–320·2
Iodine value	98·0–107·1	99·2–107·1	100·9–106·5
Refractive index at 20° C.	1·4634–1·4651	1·4627–1·4644	1·4625–1·4647

It should be pointed out that the specific gravities are abnormally high and do not agree with the specific gravities of the usual commercial rape oils, although the saponification and iodine values are within the normal limits. The specific gravity figures must, therefore, be accepted with reserve.

The percentages of ethereal mustard oil obtainable from the seeds of the above 19 *Brassica* varieties, 4 *Brassica Rapa*, and 5 *Brassica Napus* varieties, varied from 0·051 to 0·259 per cent in the seeds, and from 0·079 to 0·357 per cent in the extracted seed meal according to the determinations of C. Grimme.[1] For the corresponding percentages of ethereal oil obtained from several species of mustard seeds, see p. 264. The determinations were carried out according to the directions of the German Pharmacopœia, 5th ed.

The following table gives the characteristics of some Indian rape oils :—

[1] *Pharm. Zentralh.*, 1912 (27), 733.

Characteristics of Genuine Indian Rape Oils (Crossley and Le Sueur)

Name.	Variety.	Source.	Specific Gravity at 15.5°C. (water 15.5=1).	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent	Reichert-Meissl Value. c.c. $\frac{1}{10}$ norm. KOH.	Insoluble Acids + Unsaponifiable. Per cent.	Refractive Index at 40°C. Butyro-refracto-meter. "Degrees."	Viscosity. Seconds at 70°F.	Viscosity. Compared with Water at 70°F.	Acid Value.	Optical Activity in 200 mm. tube.
Brassica campestris	red	N.W. Provinces of India	0·9148	171·6	99·2	0·79	96 3	...	390 6	15·38	2·90	−7′
,,	glauca	,,	0·9142	171·4	97·7	0·67	95·04	59·2	402·6	15·85	1·78	−10′
,,	dichotoma	,,	0·9154	172·2	104·8	0·22	95·57	...	371·8	14·64	1·57	...
,,	...	Punjab	0·9163	173·4	96·25	0 43	94·56	...	393·2	15·48	2·57	...
,,	brown	Bombay	0·9171	172·8	94·1	0·00	...	...	464·6	18·29	4 00	...
,,	yellow	,,	0 9141	169·4	96·66	0·00	...	...	413·8	16·29	1·42	−5′
,,	napus	Bengal	0·9146	167 7	97·7	0 00	95 55	58·8	398·0	15·67	3 77	−15′
Eruca sativa allied to mustard	...	Bombay	0·9177	170·4	99·72	0·66	95 49	...	371·0	14·61	2·10	...
,,	,,	Punjab	0·9152	169·0	97·41	0 11	...	...	405 8	15·98	3 70	−11′
,,	,,	Cawnpore	0·9165	174·1	99·10	0·77	...	...	369·4	14·54	2·51	−18′

Physical and Chemical Characteristics of Rape ..

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value	
At ° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·9142 Souchère[1]			178·7	Kottstorfer Valenta	100·8-102·4	Archbutt
,,	0·9151 ²			177		97·8[4]	,,
,,	0·9150-0·917 De Negri and Fabris[1]	−10 (Summer variety)	Lewkowitsch.	170-176·4	Archbutt[3]	99·1-105·6[7]	Thomson and Ballantyne
15·5	0·9133-0·9168[7] Thomson and Ballantyne[7]	+10 (Winter variety)	,,	175[4]	,,	97·65-102·1	De Negri and Fabris
,,	0·9132-0·9159 Archbutt[3]			170·6-175·3	Thomson and Ballantyne	94·1-104·8	Crossley and Le Sueur[5]
15·5 (water 15·5=1)	0·9141-0·9177 Crossley and Le Sueur[5]			175-177	De Negri and Fabris	98-103·6	Lewkowitsch[6]
28	0·910 Dietench			177-178	Oliveri	93·5	Lewkowitsch[8]
99	0·8632 Allen			171·7-176·5	Lewkowitsch[6]	·	
(water 15·5=1)				167·7-173·4	Crossley and Le Sueur[5]		

1 Colza oil.   2 Rape oil.   3 Fifty-two samples. *Journ. Soc. Chem. Ind*, 1886, 310.
4 From Guzerat seed.   5 Indian oils; cp. p 245.   6 Commercial rape oils of good quality.
7 It should be noted that the sample giving the highest value 105·6 had the highest specific gravity 0·9168, and it is therefore open to doubt whether that sample represented genuine rape oil from cultivated seed.
8 Exceptionally fine rape oil.

Physical and Chemical Characteristics of Rape Oil—continued

Thermal Tests.

Maumené Test.

°C.	Observer.
55-64	Archbutt
51-60	Allen
49-51	De Negri and Fabris

Specific Temperature Reaction.

°C.	
125-144	Thomson and Ballantyne

Heat of Bromination.

At °C.	Observer.
18 4	Helmer and Mitchell
17·6	Jenkins
17·3	Archbutt
17-20 3	

Refractive Index.

At °C.		Observer.
15	1·4720-1·4757	Strohner
20	1·4726-1·4742	Harvey
60	1·4667	Thorner

Oleo-refractometer.

"Degrees" at 22° C.	Observer.
+15 to +18 5	Jean
+16 to +20	Pearmain

Butyro-refractometer.

At °C.	"Degrees."	Observer.
25	68	Mansfeld
40	58·8-59·2	Crossley and Le Sueur [1]

Viscosity (Redwood's Viscosimeter)

Seconds at 70° F.	Observer.
370-380	Lewkowitsch
369·4-	Crossley and
464·6	Le Sueur

[1] Indian oils.   Cp. p. 245

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Specific Gravity			Solidifying Point		Melting Point		Mean Molecular Weight		Iodine Value		Refractive Index	
Per cent.	Observer.	°C.		Observer.	°C.	Observer.	°C.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
95·1	Bensemann	99/100 (water 15·5=1)	0·8488	Allen	18·5	Allen	18·3-19·5 [5]	Allen	321·2	Allen	105·6	Williams	1·4491	Thörner
94·56-96·3	Grimme	100/100 (water 100=1)	0·8788	Archbutt	18·17	Bensemann	21-22	Bensemann [4]	307	Williams	99·8-103·1	De Negri and Fabris		
							18·5-21	Archbutt	314	Valenta	103·6 [6]	Wijs		
					16	Thörner	16-19	De Negri and Fabris						
							20	Thörner			Iodine Value of the Liquid Fatty Acids			
					Titer Test.						120·7	Wallenstein and Finck		
					12·7-13·6 [1] 11·7-12·2 [2]	Lewkowitsch					124·2-125·5 [6] 114·3 [7]	Tortelli and Ruggeri		

1 Colza oil.   2 Rape oil.   3 Point of incipient fusion.   4 Point of complete fusion.

5 Cold pressed.   6 Iodine value 102·2-101·7.   7 Very old sample, iodine value=96·4.

For further numbers cp. p. 256.

Rape seed is grown in almost all European countries. In France and in Belgium the winter variety of *Brassica Napus* is chiefly cultivated. Enormous quantities are grown in East India. The bulk of the East Indian seed is imported into England from Calcutta, Madras, Bombay, Guzerat,[1] and Ferozepore. Up to a few years ago considerable quantities of Japanese rape seed oil reached the European market. Thus in 1906, 351,400 kin[2] of oil were exported; in 1907 the export had reached 3,156,800 kin. In consequence of the large imports into Japan of Manchurian soya bean cake, the Japanese production of rape seed has greatly decreased. The following tables give the amounts of rape seed worked up by the United Kingdom, France, and Germany :—

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[1] The species yielding the Guzerat seed is known as *Brassica glauca*.
[2] 1 kin = 1⅓ lbs.

Rape Seed imported into the United Kingdom.

Countries.	1902.	1903.	1904.	1905.	1906.	1907.	1908.	1909.	1910.	1911.	1912.
	Qrs.	Qrs.	Qrs.	Qrs.	Qrs.	Qrs.	Qrs.	Qrs.	Qrs.	Qrs.	Qrs.
Russia	28,264	104,980	154,263	35,690	10,985	25,058	70,406	10,091	9,521	84,485	90,456
Germany	4,956	4,145	4,130	3,265	1,953	2,819	3,949	1,621	534	745	3,713
Holland	4,287	2,972	2,237	2,769	3,263	4,100	1,964	3,315	2,253	2,210	2,491
Belgium	1,893	107	602	4,453	3,411	982	2,531	1,379	180	2,291	1,252
France	967	330	321	1,001	757	1,512	970	1,849	214	1,326	499
Roumania	16,414	47,907	46,467	41,960	9,202	3,432	2,028	4,983	1,783	8,241	9,805
Argentine Republic	640	26	245	270	738	..	..	..	..	..	..
British India { Bombay	78,567	75,995	49,999	72,306	68,758	203,765	..	..	..	..	..
British India { Bengal	80,382	4,477	30,541	13,998	19,082	9,535	61,957	110,109	235,414	132,710	70,123
British India { Madras	8,560	67,357	19,333	5,614	..	8,995	..	..	..	..	..
Other British possessions	1,521	..	..	..	..	1,762	2,247	..	..	..	..
Japan	..	..	..	..	..	..	1,095	5,895	18	..	3
Other foreign countries	1,827	..	1,173	..	..	..	343	461	1,407	191	8,926
Total [1]	228,278	308,296	309,325	181,326	118,149	261,960	147,490	139,703	251,324	232,199	187,268

[1] The totals are the quantities actually imported; they do not represent in every case the sum of the specified items.

Rape Seed Production in France and Imports into France
(Double hundredweights)

Year.	Production.		Imports.		
	Colza.	Navette.	European Colza.	Navette.	Indian Rape Seed including Mustard Seed.
1896	.	...	64,017	27,898	460,936
1897	572,993	55,635	55,652	114,457	539,131
1898	638,236	53,507	19,244	43,164	258,104
1899	620,163	51,778	11,470	19,653	647,271
1900	425,310	35,165	150,164	452,252	299,890
1901	379,332	30,349	48,420	223,175	579,293
1902	388,943	36,489	116,095	334,452	605,226
1903	376,435	37,161	47,927	21,298	780,664
1904	527,541	54,361	22,449	2,539	580,071
1905	496,327	49,777	69,216	300,948	209,093
1906	371,005	44,876	8,126	19,080	495,687
1907	523,610		1,379	2,174	605,397
1908	560,740			414,980	
1909	590,500			589,310	
1910	519,890			849,710	
1911	461,590			780,480	
1912	?			660,730	

Rape Seed imported by Germany

(Double hundredweights)

Year	India	Russia	Other Countries	Japan	France	Roumania	Argentina	Dutch East Indies	Total
					From				
1896	35,178	42,770	12,334	...	...	...	...	...	90,282
1897	78,946	23,183	17,966	...	...	...	...	...	120,095
1898	94,752	16,566	8,973	...	...	...	...	...	120,291
1899	76,909	21,462	6,050	...	...	...	...	...	105,321
1900	62,373	22,170	47,371	...	...	...	...	...	131,914
1901	119,290	14,630	31,520	...	...	...	...	...	165,440
1902	102,480	13,650	34,460	...	...	...	...	...	150,590
1903	74,260	22,870	16,930	...	...	...	...	...	114,060
1904	117,780	8,910	6,510	...	...	...	...	...	133,200*
1905	69,890	19,530	71,540	...	...	...	...	...	160,960
1906	53,258	74,100	24,928	...	...	...	...	...	85,596
1907	140,873	79,960	7,868	...	...	...	...	...	156,737
1908	...	84,520	31,320	67,570	...	...	7,303	...	697,537
1909	1,237,468	36,718	152,850	...	22,606	42,884	...	6,490	1,427,025
1910	1,562,320	23,870	42,700	...	...	227,660	...	16,470	1,873,020
1911	1,205,250	31,820	11,420	...	...	91,260	...	5,050	1,344,800
1912	1,022,280	114,500	7,000	...	...	103,770	...	8,690	1,256,840

German Exports of Rape Seed

To	1911	1912.
Denmark	3038	2833
Holland	1919	2188
Sweden	522	629
United States of America . .	302	474

The values of the rape seed exports from India and the distribution of the exported quantities is detailed in the following table :—

Export of Rape Seed

Countries.	1899-1900.	1900-1.	1901-2.	1902-3.	1903-4.	1904-5.	1905-6.	1906-7.	1907-8.	1908-9.
	£	£	£	£	£	£	£	£	£	£
Belgium	493,711	270,214	775,272	462,607	501,992	522,611	256,896	545,082	904,634	635,645
Germany	281,026	211,184	978,322	373,814	403,556	594,912	210,200	336,237	845,558	407,703
France	413,947	170,211	785,968	474,194	464,109	405,293	125,026	453,156	674,283	368,907
United Kingdom	91,754	102,458	227,153	194,572	202,518	165,027	174,269	275,687	346,598	117,718
Italy	37,048	54,895	78,445	68,825	74,245	41,360	36,598	18,944	34,159	19,946
Holland	29,071	10,798	84,521	58,699	37,784	73,445	...	10,091	39,757	954
Other countries	346	4,070	40,722	14,713	5,203	19,867	8,948	5,511	38,737	28,662
Total	1,346,903	823,830	2,970,403	1,647,424	1,689,407	1,822,515	811,937	1,644,708	2,883,726	1,579,535

Rape seed is crushed between rollers and the meal is either expressed or extracted with carbon bisulphide or petroleum ether. The extracted oil is, as a rule, purer than the expressed oil, since a considerable amount of mucilaginous matter passes into the oil when the seed is expressed. The cakes obtained by expression form an excellent cattle food, if the seed has been tolerably pure, *i.e.* free from mustard seed and wild seeds.[1] The extracted meal is unsuitable [2] as cattle food, and is chiefly used as manure, at any rate in this country, although some meal, especially on the Continent, finds its way into compound cakes.

Rape (colza) seed contains from 33 to 43 per cent of oil. The seed harvested in the North of France contains 43 to 45 per cent; Danubian seed 38 to 40, and Indian seed from 42 to 45 per cent.

Crude rape oil is dark in colour—" brown rape oil " of commerce—and before being put on the market it is refined by treatment at the ordinary temperature with about one per cent of strong sulphuric acid (*Thénard's* process), which coagulates and carries down the impurities. At present a mixture of acid and water in equal proportions is preferred.[3] The acid must be carefully drawn off, as otherwise in the subsequent washing with water troublesome emulsions are formed ; hence conically shaped vessels are preferred for the acid treatment. The settled oil is then washed with water until free from mineral acid. The black waste acid does not seem to be recovered. *Goffart* [4] proposed to convert it into a consistent grease by heating with zinc.

The refined oil of commerce is pale yellow ; it has a characteristic smell [which may serve to identify the oil] and has, except the finest qualities, an unpleasant harsh taste. The term " colza oil " can no longer be taken as being exclusively applicable to oil expressed from the finest French seed, as was the case about forty years ago. For with the increased consumption of colza oil, rape seeds from other countries were used for the manufacture of " colza oil," especially German seed, such as rubsen seed from *Brassica campestris*, var. *rapa*. Since Indian rape seed has been introduced in European oil mills, the term " colza oil " has become a generic term, denoting a refined rape oil from the various commercial rape seeds. Therefore, the restriction of " colza oil " to a French oil or even a German oil no longer holds good, and " colza " oils are sold in trade which are made from Indian seed, such as Cawnpore seed and Guzerat seed. It should further be noted that " colza oil " was originally an oil which had been obtained by expression, and the term " best refined colza oil " must still be held as

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[1] With regard to rape cakes and their purity see G. Jorgensen, *Landw. Versuchsst.*, 1910, xxvii. 1. With regard to "greening" of rape cakes see L. Bussard, *Les Matières grasses*, 1911, 2199. Cp. also C. Brioux, *Ann. Chim. Analyt.*, 1912 (17), 3.

[2] For a process of preparing extracted rape (and ravison) seed meal for use as cattle food cp. A. W. Macllwaine and J. Caley, English patent 1853, 1899.

[3] For a refining process embracing the following operations : emulsifying oil by heating with brine, heating emulsion with a solution of sodium and zinc sulphates and tin protochloride, separating the oil and treating with potassium chlorate and hydrochloric acid, and finally treating with a 40 per cent solution of formaldehyde cp. German patent 209,128, A. van de Kerkhove.

[4] French patent 350,001.

rightly belonging to an expressed oil such as is used for edible purposes. This class of edible rape oil is largely used by bakers for greasing the ends of loaves in the oven (" bread oil "). [*Linde* [1] heats rape oil with bread crumbs or milk to about 180° C. so as to impart to it a peculiar taste.]

There are also in the market pure refined colza oils which have been obtained by extraction with solvents. These are of distinctly inferior quality ; their origin is immediately revealed by their taste. Colza oils of this class are not objectionable as burning oils,[2] but being, as stated already, of a distinctly inferior quality, they are valued in commerce at a lower figure.

Jamba oil (see p. 274) simulates rape oil, although the jamba oil is distinctly inferior in quality ; as jamba oils are now coming in large quantities on the market the distinction between rape oils and jamba oils has gained some importance (see p. 274).

Saturated fatty acids occur in rape oil to a small amount only. *Tolman and Munson* found by the lead-salt-ether method 1·02 per cent (and less) of solid fatty acids. What *Reimer and Will* [3] termed behenic acid in rape oil has been shown by *J. E. Alén* [4] *and Ponzio* [5] to be in reality crude arachidic acid (*i.e.* a mixture of arachidic acid and lignoceric acid). *Archbutt* [6] confirmed the occurrence of " arachidic acid " in a number of commercial rape oils. His determinations are reproduced in the following table :—

Origin of Oil.	Crude Arachidic Acid.	
	Per cent.	Melting Point. °C.
Crude, several years old, from Rubsen	0·59	69·2
Crude, several years old, from Raps	0·36	69·0
Kustendje (Black Sea)	0·84	70·4
Refined, Stettin	1·14	69·0
	After purification by one recrystallisation from 90 per cent alcohol,	
	0·91	72·2
Oil prepared in the Laboratory from Guzerat seed	1·61	71·1
	After purification by twice recrystallising from 50 c.c. of 90 per cent alcohol,	
	1·43	73·1

Amongst the unsaturated fatty acids, erucic and rapic acids have been identified. On subjecting the mixed fatty acids to the lead-salt-

[1] United States patent, 692,187.
[2] Rape oil imported to Australia as " burning oil " must be denatured with 5 gallons of " blown " rape oil (see Vol. III. Chap. XV.) and 10 oz. of birch tar oil (of spec. grav. 0·926) at 20° C. per 100 gallons of oil.
[3] *Berichte,* 1887, 2388.
[4] *Svensk Kemisk Tidskrift,* 1892, 78 ; 1893, 179.
[5] *Journ. f. prakt. Chem.,* 1893 [48], 487 ; *Journ. Soc. Chem. Ind.,* 1894, 257.
[6] *Journ. Soc. Chem. Ind.,* 1898, 1009.

ether process of resolving the mixed fatty acids into " solid " and " liquid " acids, erucic acid remains to a large extent with the solid acids. Hence the " solid " acids of rape oil obtained by this method are characterised by a high iodine value, 62, and low melting point (cp. Vol. I. pp. 544 and 553). For the detection and estimation of erucic acid see Vol. I. p. 553. Since the iodine value of the unsaturated liquid fatty acids lies in the neighbourhood of 120, whereas the respective iodine values of rapic and erucic acids are 90·07 and 75·15, the presence of unsaturated fatty acids belonging to the linolic, or to the linolenic series must be suspected. Indeed *Hehner and Mitchell* obtained 3·6 per cent of a brominated acid melting at 179° C.; the same compound was also isolated by *Farnsteiner*, and by *Walker and Warburton* in the author's laboratory; the last-named observers obtained 2·4 to 3·4 per cent of ether insoluble bromide.

On standing, " stearine " separates from rape oil at the ordinary temperature. A specimen of rape " stearine " gave the following result (*Halenke and Moslinger* [1]) :—

	Melting Point. °C.	Saponification Value.
Fat	38·5	161·76
Fatty acids . .	34	160·05

It follows from these numbers that the " stearine " consisted practically of trierucin only.

Reimer and Will [2] obtained from a specimen of crude rape oil " stearine," by dissolving the solid mass in ether, filtering and precipitating with alcohol, colourless needles melting at 47° C. These consisted of pure dierucin. The formation of dierucin is due to hydrolysis of the oil having been arrested at the first stage [3] (see Vol. I. Chap. II.).

According to *Normann*,[4] dierucin, although frequently met with in crude oil, has never been found in refined oil.

The amount of the unsaponifiable matter contained in rape oil varies from 0·5 to 1 per cent. This figure is rarely exceeded. Rape oils containing larger amounts of unsaponifiable matter, exceeding 2 per cent, should be looked upon with suspicion. According to *Windaus and Welsch* [5] the " phytosterol " from rape oil consists of a mixture of brassicasterol (Vol. I. p. 278) and of a " phytosterol " which is similar to, but not identical with, sitosterol; the alcohol melted at 142° C. (whereas sitosterol melts at 136°-137° C.), and its acetate at 134° C.; its propionate at 116° C., cinnamate at 151° C., and benzoate at 143° C.

It appears that *Siegfeld* [6] had the brassicasterol acetate in his hands, for after having prepared the " rape oil phytosteryl " acetate, melting

[1] *Corresp. d. Vereins d. bayer. Chem.* No. 1.
[2] *Berichte*, 1886, 3320.   [3] Cp. C. L. Reimer, *Berichte*, 1907, 256.
[4] *Chem. Zeit.*, 1907, 211.   [5] *Berichte*, 1906, 4378.
[6] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1904 [vii.], 581.

after thé fifth crystallisation at 135·5° C.–136·5° C., he found in the mother liquors an acetate melting after the thirteenth crystallisation at 145·6° C.–146·6° C.

Commercial rape oil as a rule contains free fatty acids. In view of the importance which the proportion of free fatty acids has on the valuation of commercial rape oils intended for lubricating purposes and for burning, I collate in the following table some observations :—

Free Fatty Acids in Rape Oils

Description of Oil.	No. of Samples.	Free Fatty Acids in terms of Oleic Acid.	Observer.
		Per cent.	
Edible oil	3	0·53–1·82	Nördlinger
Commercial oil, expressed .	9	0 52–6·26	,,
,, ,, extracted .	2	0·77–1·1	,,
,, ,, . . .	5	2 43 6·24	Thomson and Ballantyne
,, ,, . . .	50	1·7–5·5	Archbutt
,, ,, . . .	5	1·05–3·9	Deering
Indian oils	10	0·7–2·01	Crossley and Le Sueur
		0·7–5·2	Lewkowitsch

Rape oil absorbs in *Livache's* test 2·9 per cent of oxygen after seven days, whereas the fatty acids absorb only 0·9 per cent after eight days. The oil thickens and becomes rancid without, however, drying. Rape oil may, therefore, be considered as representing a class of oils occupying an intermediate position between the semi-drying and the non-drying oils.

It is most likely due to this slight drying power that old rape oil samples exhibit notable acetyl numbers. Thus *Lewkowitsch* found in a sample of old colza oil the acetyl value 14·7, and *Gripper* values varying from 24 to 41·7.

The following table, due to *Gripper*,[1] gives the characteristics of a number of old rape oils which had been kept in corked bottles in full daylight for the times stated. For comparison, the numbers obtained for fresh rape oil are added. It appears that air had access to the oil, as the specific gravities and viscosities, as also the acetyl numbers and soluble fatty acids, had increased, whilst the iodine values had decreased.

[1] *Journ. Soc. Chem. Ind.*, 1899, 342.

	Specific Gravity at 60° F.	Free Fatty Acids as Oleic Acid Per cent.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Insoluble Acids + Unsaponi-fiable.	Soluble Fatty Acids equivalent to per cent KOH.	Viscosity at 60° F. Rape Oil at 60° F. =100.	Insoluble Fatty Acids.			
									Melting Point °C.[1]	Molecular Weight.	Iodine Value.	Acetyl Value.
Rape oil, 8 years 9 months old	0·9356	13·35	197·2	63·89	20·2	89·1	3·48	1163	21·1	326·1	72·07	41·73
,, 6 ,, 6 ,,	0·9478	8·19	195·7	70·83		90·34	...	750 (about)	16·7	320·0	...	...
,, 7 ,, 5 ,,	0·9441	7·98	194·3	72·06	15·7	90·17	2·80	587	18·1	320·0	79·06	38·78
,, 7 ,, 10 ,,	0·9414	11·04	183·4	71·52	...	89·91	2·47	515	17·2	320·0	77·28	35·39
,, 9 ,, 1 ,,	0·9265	6·76	180·9	83·37	.	92·90	1·63	214	20·0	324·6	86·02	28·72
,, 10 ,, 1 ,,	0·9287	8·33	180·6	90·38		92·67	1·51	245	18·3	314·4	...	...
,, 4 ,, 8 ,,	0·9196	4·22	179·4	94·35		94·34	1·12	145	18·1	320·5	98·23	...
,, 8 ,, 2 ,,	0·9197	5·62	191·7	98·90	...	94·07	0·95	131	16·1	320·5	103·93	25·71
,, 9 ,, 8 ,,	0·9156	4·82	176·7	98·64	...	95·04	0·67	115	17·8	329·0	...	...
,, 4 ,, 0 ,,	0·9142	4·30	178·0	96·92	4·2	95·70	0·67	110	18·3	320·5	...	...
,, 6 ,, 0 ,,	0·9170	5·74	180·4	101·34		96·00	0·78	104	17·2	324·6	107·12	28·94
,, 5 ,, 2 ,,	0·9167	4·32	178·6	100·35	..	95·70	0·69	102	19·1	320·5	104·17	24·45
Rape oil, fresh	0·9140	2·70	177·8	99·08	...	95·60	0·39	100	20	...	...	23·11

[1] Determined by Crossley and Le Sueur's method (Vol. I. p. 321).

The changes which rape oil undergoes on blowing with air at 100° C. have been investigated by *Procter and Holmes*.[1] Their results are reproduced in the following table :—

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
Hours.			
0	0·911	1·4748	120·0
3	0·913	1·4749	97·0
6	0 913	1·4750	94·0
9	0·913	1·4750	90·0
12	0·913	1·4751	89·0
15	0·914	1·4754	89·0
18	0·915	1·4756	88·0
21	0·919	1·4756	87·0
24	0·922	1·4758	86·0

In the elaïdin test rape oil does not give characteristic indications.

Rape oil is largely adulterated according to market prices with one or more of the following fatty oils : linseed (hemp seed), poppy seed, cameline, cotton seed, ravison, hedge mustard oils, and also with refined fish and blubber oils. Paraffin and rosin oils are also frequently added fraudulently.

In order to " correct " the specific gravity, which may have been raised by the addition of the last named two unsaponifiable oils, sperm oil is also added. Paraffin and rosin oils are easily detected by estimating the amount of *unsaponifiable matter*. The presence of sperm oil also increases the amount of unsaponifiable matter, as it yields on saponification 37 to 41 per cent of unsaponifiable substances. Hence, the examination of the unsaponifiable matter for the presence of sperm oil alcohols may become necessary in special cases. (Cp. Vol. I. Chap. IX. p. 601).

The addition of large quantities of linseed, hemp seed, poppy seed, cameline, fish and blubber oils is readily recognised by a high iodine value, and chiefly by determining one of the following characteristics : specific gravity, melting point of the fatty acids, thermal tests, saponification value, and also the viscosity of the oil.

The **specific gravity** of rape oil rarely exceeds 0·916, and this may be considered for practical purposes as the limit, although, as will be seen from the table given above, higher values have been recorded. Thus, of fifty-two samples examined by *Archbutt*—

7 samples had a specific gravity below 0·9140
27   „   „   „   above 0·9139 but below 0·9150
18 ·   „   „   „   „   0·9149   „   0·9160

The specific gravities of the other fatty oils that may be used as adulterants being higher than 0·9160, a sample of oil the specific gravity

[1] *Journ. Soc. Chem. Ind.*, 1905, 1287.

of which exceeds that figure must be looked upon with suspicion. Of course, presence of an unsaponifiable oil cannot be detected by determination of the specific gravity alone ; it has been pointed out already that the specific gravity of an adulterated oil is usually " corrected." (For abnormally high specific gravities of some rape oils prepared on a small scale see table, p. 262.)

The **melting point of the fatty acids** and the **solidifying point** (titer test) of an adulterated sample is higher than the normal one if cotton seed oil has been added ; on the other hand, it is lowered by the presence of linseed oil or of any of the other oils mentioned above. If cotton seed oil be suspected, the *Halphen* colour reaction may be used as a confirmatory test. In case heated cotton seed oil had been used, this test will fail. The nitric acid colour test is too uncertain in the presence of rape oil.

The **thermal test** with sulphuric acid or bromine [1] is still largely used, although the indications furnished by the iodine value are much more reliable. The thermal reactions indicate admixture of linseed or other drying oils, or semi-drying oils, such as cotton seed oil.

The **saponification value** of the sample under examination will easily lead to a decision as to whether any other fatty oil, with *the exception of an oil belonging to the rape oil group, such as ravison or hedge mustard oil,* is present to a notable extent. Owing to the large proportion of erucic acid in rape oil, its saponification value is very low, lower than that of any of the fatty oils mentioned above. [Castor oil, which is also characterised by a low saponification value, would be detected by the specific gravity and high acetyl value of the suspected sample.] It should, however, not be forgotten that a low saponification value results also in the presence of unsaponifiable oils. In that case the latter must be separated first, and the neutralisation value of the fatty acids is determined subsequently.

The following are the saponification values of the fifty-two samples of rape oil examined by *Archbutt* :—

4 samples	170 to	171
12 „	171 „	172
9 „	172 „	173
14 „	173 „	174
11 „	174 „	175
1 „	175 „	176
1 „	176 „	177

It may be repeated that the other members of the rape oil class also have low saponification values.

The determination of the **iodine value** should not be omitted, for this number affords valuable guidance as to the presence of oils which belong to the rape oil group but are not derived from the cultivated seed. Such oils (ravison oil, etc.), cannot be detected by the saponification value alone, but are indicated by somewhat high iodine values,

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[1] Cp. Archbutt, *Journ. Soc. Chem. Ind.*, 1897, 311.

especially if the latter be associated with high specific gravity numbers. The figures given in the table of "characteristics" under the heading "iodine value," as also the numbers given in the following table, will furnish further information :—

Characteristics of Genuine Rape Oils and Allied Oils (Lewkowitsch)

	Specific Gravity at 60° F. (water at 60°=1)	Saponi-fication Value.	Iodine Value.	Viscosity.		Un-saponifiable Matter. Per cent.
				At 70° F.	At 140° F.	
Genuine rape oil, crude .	0·91458	173·1	106·8			
,, ,, refined .	0·91364	173·1	104·4	380		
,, ,, ,, East Ind.	0·9139	172·9	102·1			
,, ,, ,, ,, .	0·9139	168 8	104·2	...	...	1·69
,, ,, ,, .	0·9115	173·2	103·6	375	...	3·13
,, ,, ,, .	0·9146	172	103·5	..	94	
,, ,, ,, .	0·9147	173	104·6	...	92	1·43
,, ,, ,, .	0·9147	172·5	103·1	...	94	1·56
,, ,, ,, .	0·9153	176 6	102·9	...	91	1·42
German "colza" oil contain-ing mustard seed oil .	0·9161	175·3	106·5			
Rape oil, second quality .	0·91629	175·8	110 3	360		
Ravison oil [1] . .	0 91793	177·1	114 7	329		
,, ,, . .	0·9204	178 5	120·4	331	...	2·29

It may be added that the iodine numbers 98-103·6 given by the author in the table of "characteristics" have been derived from a special investigation of a very large number of genuine rape oils (from cultivated seed). The number 93·5 given in that table is exceptionally low.

The determination of the **viscosity** of rape oil is a very valuable means of ascertaining its purity. It will be found best in an examination to compare the sample with a standard rape oil of known purity, as the viscosity of rape oil is fairly constant. Since no other oil likely to be used as an adulterant, with the exception of castor oil, possesses so high a viscosity as rape oil, the genuineness of the sample can thus be ascertained.

The **Valenta** test is very characteristic of rape oil, and proves useful as an additional means of deciding whether a sample is genuine or not.

Fish oils and **blubber oils** in rape oil may be recognised by their peculiar smell and taste, especially on warming, and also by the intensity of the phospho-molybdic acid reaction. More important evidence will be furnished by the determination and examination of the ether-insoluble bromide prepared from the mixed fatty acids. (Separation of octo-bromide, see Vol. I. p. 573.) Confirmatory evidence will be furnished by the phytosteryl acetate test (cp. "Linseed Oil," p. 69), as also by the iodine value of the oil and of its liquid fatty acids.

[1] Cp. also "Ravison Oil," p. 241.

Since rape oil is refined with sulphuric acid, commercial oils should be tested for the presence of sulphuric acid by shaking the oil with warm water and examining the aqueous layer.

The detection of rape oil in *other oils* by means of colour reactions (such as *Mailho's* or *Schneider's* reagents), purporting to show presence of sulphur, can no longer be considered as useful. The " cold-drawn " oils of commerce are entirely devoid of sulphur, but oils extracted by means of carbon bisulphide may retain some sulphur, it being difficult to remove the last traces of the solvent. The colour reaction proposed by *Palas* [1] for the detection of rape oil in olive oil (viz. agitation with rosaniline sulphite) is valueless, as experiments made by the author have shown.

Rape oil in other oils is detected by its characteristic smell and taste, and by the influence it exercises on the characteristics of the oil under examination, such as the iodine value of the oil, the iodine value of the liquid fatty acids, and chiefly on the saponification value.

" Cold-drawn " rape oil is used as an edible oil, especially in India. It is also used as an edible oil on the Continent, and in this country as " bread oil " (see p. 256). Those colza oils which are unsuitable for edible purposes find an outlet as excellent burning oils. Equally well-refined oils can also be used as wool oils. Enormous quantities of rape oil are used for lubricating purposes both in the refined state, and as " blown rape " oil (see Vol. III. Chap. XV.). Smaller quantities are used on the Continent for the making of soft soap, but as a rule rape oil can hardly be termed a suitable soapmaking oil. Rape oil is also largely used for quenching steel plates.

BLACK MUSTARD SEED OIL

French—*Huile de moutarde noire.*   German—*Schwarzsenföl.*
Italian—*Olio di mostarda nera.*

For table of characteristics see pp. 266, 267.

Black mustard seed oil is obtained from the seeds of *Sinapis nigra*, L. (*Brassica nigra*, Koch), which contain 31-33 per cent of oil. (*Grimme* found 28·3 per cent.) The oil has a brownish-yellow colour and a mild taste ; it smells of ethereal mustard oil. *Grimme* [2] obtained from the seeds 0·995 per cent, and from the solvent extracted seed meal 1·388 per cent of ethereal mustard oil.

In its chemical composition it closely resembles rape oil. *Tolman and Munson* obtained from various samples by the lead-salt-ether method from 2·32 to 4·05 per cent of solid fatty acids containing arachidic acid. Amongst the unsaturated acids erucic and a liquid fatty acid [3] (rapic acid ?) have been found.

[1] *Journ. Soc. Chem. Ind.*, 1897, 361.   [2] *Pharm. Zeit.*, 1912, 520.
[3] Goldschmiedt, *Weiner Berichte*, 70 [2], 451.

The oil is obtained as a by-product in the manufacture of ethereal mustard oil. It is not suitable for burning, and therefore is chiefly used for soap-making. Efforts have been made lately to introduce this oil, under the name " Sinapol," for cosmetic and pharmaceutical purposes, as a substitute for olive oil.

In Calcutta very large mills, driven by steam power, produce the oil in (native) grinding mortars (" checcos "). The oil is used largely for edible purposes. No hydraulic presses are employed, the reason being that the native mills require no important capital outlay. Moreover the native mills give almost the same yield as hydraulic pressing would give.

Suzzi described two species of black mustard seed oil cultivated in Italian East Africa (Erythrea), viz. *Brassica nigra* and *Brassica carinata*, the seeds of which contain 29·75 and 29·74 per cent of oil respectively. The characteristics of the two oils were the following :—

	Oil from *Brassica nigra*.	Oil from *Brassica carinata*.
Specific gravity at 15° C. . . .	0·9175	0·917
Saponification value . . .	176·5	175·2
Iodine Value	116·1	112·7
Maumené test	77° C.	74° C.

Fatty Acids

Melting point[1]	16·2° C.	
Neutralisation value . . .	179·2	179·5
Saponification value . . .	181·1	182·0

Indian mustard seed from *Brassica juncea*, D.C. = *Brassica juncea*, Hooker fils et Thomson (a variety of *Sinapis nigra*) is extensively cultivated and is known in India as " *rai*." [2] This seed yields the " Sarepta " mustard. Russian mustard, and generally all European mustard, is derived from *Brassica Besseriana*, .Andrz. *Crossley and Le Sueur* give the following numbers from mustard seed oil from " *rai*":—

Specific gravity at 15·5°/15·5° . . .	0·9158
Saponification value . . .	172·1
Iodine value	101·8
Butyro-refractometer " degrees " . .	60

Mustard oil imported from India is sometimes adulterated; a specimen examined contained considerable amounts of sesame oil. *Grimme*,[3]

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[1] Crossley and Le Sueur's method (Vol. I. p 321).
[2] " Rai," *Brassica juncea* as distinct from " sarson," *Brassica campestris*.
[3] *Pharm. Zeit.*, 1912, 520 ; cp. also L. Farcy, *Ann. d. Falsific.*, 1912 (5), 528.

who obtained 33·3 per cent of oil from the seeds, gives the following characteristics :—

Oil—

Specific gravity at 15° C.	.	.	.	0·9206
Solidifying point, ° C.	.	.	.	– 11 to – 12
Saponification value	.	.	.	174·4
Iodine value	.	.	.	106·8
Refractive index at 20° C.	.	.	.	1·4723

Fatty Acids—

Fatty acids, per cent	.	.	.	94·27
Unsaponifiable matter, per cent	.	.	.	1·04
Solidifying point, ° C.	.	.	.	13·15
Melting point, ° C.	.	.	.	17·18
Neutralisation value	.	.	.	177·7
Mean molecular weight	.	.	.	315·8
Iodine value	.	.	.	109·3
Refractive index at 20° C.	.	.	.	1·4627

The seeds yielded 1·137 per cent and the extracted seed meal 1·705 per cent of ethereal mustard oil.

Physical and Chemical Characteristics of Black Mustard Seed Oil

Origin.	Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.	
	At °C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
Bengal	15 15·5 (water =1)	0·9212 (?) 0·9155	Grimme[3] Crossley and Le Sueur[2]	−15 to −16	Grimme	173·2 173·3	Grimme Crossley and Le Sueur	101·1 98·84	Grimme Crossley and Le Sueur
Central Provinces	15·5 „	0·9185 0·9170-0·9193	Tolman and Munson			173	„	103·6 105·8-113	Blasdale[1] Tolman and Munson
India	20	0·9143·	Wijs			175·8	Wijs	122·3 110·51	Wijs Lewkowitsch

Physical and Chemical Characteristics of Black Mustard Seed Oil—continued

Maumené Test.		Refractive Index.		Viscosity.	
°C.	Observer.	At °C.	Observer.	Seconds at 70° F.	Observer.
42-43 58·5 (1)	De Negri and Fabris Lengfeld and Paparelli	15·5 20	1·4672 1·4739	Tolman and Munson Grimme	425·4 355·4	Crossley and Le Sueur „
		15·5	Butyro-refractometer "Degrees." 76·5 59·5	Tolman and Munson Crossley and Le Sueur		

[1] *Journ. Soc. Chem. Ind.*, 1896, 206.
[2] *Journ. Soc. Chem. Ind.*, 1898, 991.　The two samples had the acid values 7·35 and 5·72 respectively, and the optical activity, in
[3] 200 mm. tube, −0° 17' and −0° 30' respectively.
[4] The specific gravity number is abnormally high and has therefore been queried.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Solidifying Point		Melting Point		Iodine Value		Neutralisation Value		Mean Molecular Weight		Refractive Index	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.		Observer.	At 20° C.	Observer.
95·05	Crossley and Le Sueur			16-17	De Negri and Fabris	109·6	De Negri and Fabris						
95·32[1]	Grimme	6-8	Grimme	15 9-10	Blasdale Grimme	126·5 108·4	Wijs Grimme	187·1 176·7	Wijs Grimme	299·8 317·8	Wijs Grimme	1·4665	Grimme
							Liquid Fatty Acids.						
						119·8	Tolman and Munson						

[1] 94·16 per cent fatty acids and 1·18 per cent unsaponifiable matter.

WHITE MUSTARD SEED OIL

French—*Huile de moutarde blanche.*   German—*Weisssenfol.*
Italian—*Olio di mostarda bianca.*

For tables of characteristics see pp. 269, 270.

White mustard seed oil is obtained from the seeds of *Sinapis alba*,
L. (*Brassica alba*), which contain 25-26° per cent of an oil of golden-
yellow colour, and having a burning taste.   The seed gave (*Grimme* [1])
0·827 per cent and the extracted seed meal 1·150 per cent of ethereal
mustard oil.

Most of the physical and chemical characteristics are almost identical
with those of black mustard oil.   The iodine values, however, appear
to differ considerably.   This agrees with *Tolman and Munson's* state-
ment that this oil yields only traces of solid acids by the lead-salt-ether
method.   *Hehner and Mitchell* obtained 1·5 per cent of an ether insoluble
bromide from a specimen of white mustard seed oil.

A sample examined by *Archbutt* [2] yielded 1·18 per cent of crude
arachidic acid, of the melting point 69° C.

The oil is used as a burning and lubricating oil.

[1] *Pharm. Zeit.*, 1912, 521.
[2] *Journ. Soc. Chem. Ind.*, 1898, 1009.

Physical and Chemical Characteristics of White Mustard Seed Oil

Specific Gravity			Solidifying Point		Saponification Value		Iodine Value	
°C		Observer	°C	Observer	Mgrms. KOH	Observer	Per cent	Observer
15	0·9125-0·9160	De Negri and Fabris	-16·3	Chateau	170·3-171·4	De Negri and Fabris	92·1-93·8	De Negri and Fabris
15	0·9151	Blasdale			173·9	Blasdale	97·68	Lengfeld and Paparelli
15·5(water 15·5=1)	0·9142¹	Crossley and Le Sueur			171·2	Crossley and Le Sueur	99·4	Blasdale
20	0·9121	Wijs			174·6	Wijs	96·75	Crossley and Le Sueur
15	0·9214	Grimme	-15 to -16	Grimme	177·8	Grimme	103	Wijs
							96·8	Grimme

Physical and Chemical Characteristics of White Mustard Seed Oil—continued

Maumené Test		Refractive Index			Viscosity	
°C	Observer	°C		Observer		Observer
44·45	De Negri Fabris	15·5	1·4750	Tolman and Munson	Seconds at 70° F.	
49·5	Lengfeld and Paparelli	20	1·4704	Grimme		
		Butyro-refractometer "Degrees."				
		15·5	74·5	Tolman and Munson	402	Crossley and Le Sueur
		40	58·5	Crossley and Le Sueur		

¹ Indian oil (*Journ. Soc. Chem. Ind.,* 1898, 991); the acid value of this specimen was 5·40 ; its optical activity in a 200 mm. tube -0° 9'.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable		Solidifying Point °C.	Melting Point °C.	Iodine Value Per cent.	Observer	Neutralisation Value		Mean Molecular Weight		Refractive Index	
Per cent.	Observer					Mgrms KOH	Observer		Observer	20° C.	Observer
96·7	Lengfeld and Paparelli		15-16	94·7-95·87	De Negri and Fabris						
95·86	Crossley and Le Sueur		16	106·2	Blasdale						
					Wijs	185·8	Wijs	301·9	Wijs		
95-21[1]	Grimme	9·10°	12-13	110·4	Grimme	181	Grimme	310·3	Grimme	1·4630	Grimme
				Liquid Fatty Acids 103·1	Tolman and Munson						

1 Fatty acids 94·23 ; unsaponifiable matter 0·98 per cent.

Grimme examined the oils from the following four varieties of mustard seed :—

Sinapis arvensis, L. ; *Sinapis chinensis*, *Sinapis dissecta*, and *Eruca sativa*.[1] The characteristics found by *Grimme* are reproduced in the following table :—

	Sinapis arvensis,[2] L.	*Sinapis chinensis*, L.	*Sinapis dissecta*, L.	*Eruca sativa*, Link.
Oil—				
Specific gravity at 15° C.	0·9228	0·9230	0·9221	0·9198
Solidifying point	− 13 to − 15°	− 14°	− 13 to − 14°	− 8 to − 10
Saponification value	179·4	177·3	178·2	174·4
Iodine value	102·6	103·3	105·6	101·8
Refractive index at 20° C.	1·4738	1·4736	1·4725	1·4723
Fatty Acids—				
Fatty acids, per cent	94·21	94·28	94·34	94·24
Unsaponifiable matter, per cent	1·12	0·96	0·96	1·07
Solidifying point	4·5°	14·15°	5·8°	8·10°
Melting point	6·8°	17·18°	9·10°	12·13°
Neutralisation value	179·8	182·0	181·7	180·1
Mean molecular weight	312·4	308·6	309·1	311·8
Iodine value	106·6	106·7	109·0	103·6
Refractive index at 20° C.	1·4625	1·4648	1·4645	1·4643

The percentages of ethereal mustard oil obtained from the seeds of the above species are given in the following table :—

Name.	Ethereal Mustard Oil Seed.	Ethereal Mustard Oil in Extracted Seed Meal.
	Per cent.	Per cent.
Sinapis arvensis	0·959	1·308
Sinapis chinensis	1·407	2 022
Sinapis dissecta	0 833	1·150
Eruca sativa	1·075	1·586

[1] Cp. S. Hals and J. F. Gram, *Landw. Versuchsst.*, 1909 (70), 307 :—"On the seeds of Eruca sativa."

[2] This plant is known as wild mustard charlock, the seeds of which yield an oil known as *charlock oil*. The oil itself is not a commercial article, since the endeavour of the rape seed growers is directed to the destruction of the charlock plant as being a weed.

RADISH SEED OIL

French—*Huile de raifort.*   German—*Rettichöl.*
Italian—*Olio di ravano (ravanello).*

For tables of characteristics see p. 273.

Radish seed oil, which, like the two preceding oils, closely resembles
rape oil, is obtained from the seeds of *Raphanus sativus*, L.[1] (rat-tail
radish), which contain from 45 to 50 per cent of oil.   The green colour
said to be characteristic of the soap solution of hedge mustard oil is not
observed when the oil is saponified (*De Negri and Fabris*).   ·

An Indian oil from Assam of the acid value 14·5 (*Crossley and Le
Sueur* [2]), was described as a *non*-drying oil.

Grimme examined the oil from four varieties of *Raphanus sativus*,
L., viz. *R. s. albus*, L.; *R. s. niger*, D.C.; *R. s. Radiola*, D.C.; and
R. s. oleiferus.   The characteristics of these four oils vary within the
limits given in the table on p. 273.

[1] For the enzymic action of raphanus sativus cp. T. Saiki, *Zeitschr. f. physiol. Chem.*,
1906, 48, 469.
[2] *Journ. Soc. Chem. Ind.*, 1898, 991.

Physical and Chemical Characteristics of Radish Seed Oil

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Maumené Test		Refractive Index		Viscosity	
At °C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C	Observer.	At 20° C.	Observer.	Seconds at 70° F.	Observer.
15 water at 15=1 15 0·9175	De Negri and Fabris	−10 to −17·5	Schaedler	178 05	De Negri and Fabris	95 6-95 9	De Negri and Fabris	51	De Negri and Fabris				
0·9165-	Grimme	−10 to −14	Grimme	179 6-	Grimme	99·8-	Grimme			1·471- 1·4722	Grimme		
15·5 water at 15·5=1 20 0·9178 0·9163	Crossley and Le Sueur			181 6 173 8	Crossley and Le Sueur	103·5 92 85	Crossley and Le Sueur			Butyro-refractometer at 40° C. "Degrees" 57·5	Crossley and Le Sueur	385·3	Crossley and Le Sueur
0·9142	Wijs[1]			179·4	Wijs	112·4	Wijs						

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value.		Neutralisation Value.		Mean Molecular Weight.	Refractive Index.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	Observer.	at 20° C.	Observer.
95·94	Crossley and Le Sueur	13-15	De Negri and Fabris	20	De Negri and Fabris	97 1	De Negri and Fabris	189 5	Wijs	296 Wijs	1·4625- 1·4630	Grimme
94 99- 95·01	Grimme	7-11	Grimme	11-15	Grimme	115·3 102 4- 108	Wijs Grimme	182 6- 185 6	Grimme	302 6- 307·6 Grimme		

1 Zeits. f. Unters. d. Nahrgs- u. Genussm, 1903, 492.

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JAMBA OIL [1]

French—*Huile de Jamba.*   German—*Jambaöl.*
Italian—*Olio di Jambo.*

For tables of characteristics see p. 275.

Jamba oil, obtained from the seeds of a plant belonging to a variety of the genus *Brassica,* is closely related to rape oil.   The seeds contain about 26 per cent of oil.

The oil behaves somewhat abnormally in that it does not lend itself readily to the manufacture of " blown " oil, as the specific gravity of the oil does not rise by " blowing " at the same rate as that of other oils belonging to the rape oil group.   A further instance of its abnormal behaviour is that the temperature does not rise spontaneously when the source of heat has been removed.

A sample examined in the author's laboratory contained 0·45 per cent unsaponifiable matter ; it yielded 1·05 per cent of fatty acids insoluble in petroleum ether.   *Thomson and Dunlop* [2] found 1·02 per cent of unsaponifiable matter.

Jamba oil is distinctly inferior to the rape oils made from genuine rape seed (see p. 256), a difference which finds its expression in the commercial value of the oil, which is generally twenty to thirty shillings per ton lower in price than refined colza oil.

Jamba oil is recognised by its peculiar taste and smell.   It may be considered a good burning oil, but does not burn as well as colza oil (cp. Vol. III. Chap. XV.).   It is, however, a distinctly better burning oil than ravison oil, and, in this respect, takes its place between ravison oil and best Indian rape oil.

[1] De Negri and Fabris, *Ann. d. Lab. Chim. delle Gabelle,* 1891–92, 137.
[2] *Analyst,* 1906, 282.

Physical and Chemical Characteristics of Jamba Oil

Specific Gravity.	Solidifying Point.	Saponification Value.	Iodine Value.	Maumené Test.	Refractive Index. Butyro-refractometer.		Observer.
15° C	° C.	Mgrms. KOH.	Per cent.	° C.	° C.	"Degrees."	
0·9150-0·9158	−10 to −12	172·26	95·2-95·6	51-53	25		De Negri and Fabris
0·9151	...	174·8	101·3-103·5	...		67·2	Lewkowitsch
		175·3	98·3	...			Thomson and Dunlop[1]

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.	Solidifying Point.	Melting Point.	Neutralisation Value	Mean Molecular Weight.	Iodine Value.	Observer.
Per cent.	° C.	° C.	Mgrms. KOH.		Per cent.	
...96·52	16-11	19-21	173·8-174	...305	96·1-96·2	De Negri and Fabris Lewkowitsch

[1] *Analyst*, 1906, 282.

Lesser-known Oils from Cruciferæ

OILS

Name of Oil	German	Source	Yield	Specific gravity at 15° C.	Solidifying Point	Saponification Value	Iodine Value (Wijs)	Refractive Index	Observer
			Per cent.		° C.				
Water cress	Brunnenkressenol	Nasturtium officinale, R. Br.	24 0	0·9205	-5 to -6	170·9	98 6	1·4704 (20° C.)	Grimme
Winter cress	Winterkressenol	Barbarea praecor, R. Br.	20 3	0·9214	-5 to -7	180 0	137 3	1·475 (20° C.)	„
Sea kale	Meerkohlol	Crambe maritima, L.	47 0	0·9187	-8 to -10	179·5	92 7	1·4715 (20° C.)	„
Spoonwort	Löffelkrautol	Cochlearia officinalis, L.	22 5	0 9232	-7 to -8	173·4	143·3	1·4739 (20° C.)	„
Hedge mustard	Hederichol	Raphanus Raphanistrum, L.	21 5	0 9186	-13 to -14	176·0	105·0	1·4722 (20° C.)	Valenta
Woad	Farberwaidol	Isatis tinctoria, L.	35-40 / 31 3	0 9175 / 0 9251	-8 / -2 to -3	174 / 181·2	105 (Hübl) / 111 8	... / 1·4751 (15° C.)	Grimme

FATTY ACIDS

From	Insoluble Fatty Acids + Unsaponifiable	Unsaponifiable Matter	Melting Point	Solidifying Point	Neutralisation Value	Iodine Value (Wijs)	Mean Molecular Weight	Refractive Index
	Per cent.	Per cent.	° C.	° C.				25° C.
Water cress	94 28	1 11	24-25	21-22	174·0	102 5	322 7	1·4621
Winter cress	94 42	0 98	23-24	21-22	180·4	139 2	296·5	1·4666
Sea kale	93 15	2 22	18-20	16-18	181·5	99·3	309·4	1·4673
Spoonwort	94 52	1 05	14-16	15-16	179·1	139·2	313·6	1·4670
Hedge mustard	94 33	1 30	14-16	15-16	179·5	109·1	312·8	1·4658
Woad	92 81	2 86	24-25	21-22	191·0	121·2	294·0	1·4710

(3) Non-Drying Oils

The oils enumerated under this heading are characterised by lower iodine values than those exhibited by the members of the two preceding classes. Linolenic acid is completely absent; linolic acid is present in small quantities only. The oils which stand at the head of this section up to and including peach kernel oil still possess slight drying properties. Owing to the predominance of olein the non-drying oils solidify on treatment with nitrous acid, yielding hard elaïdins; castor oil gives under these conditions solid ricinelaïdin.

It should be noted that the property of not drying holds good for these oils at the ordinary temperature only; at higher temperatures the non-drying oils become viscous and thicken. The chemical changes then taking place have not yet been investigated.

Castor oil (and also grape seed oil, which seems to be related to it) has been placed at the end of this class, on account of its being a most markedly non-drying oil. The chemical composition of castor oil (and pending further confirmation also of grape seed oil) differs totally from that of all other fatty oils; for this reason it appears justifiable to form a separate group of castor oil and grape seed oil.

QUINCE OIL

French—*Huile de coing.* German—*Quittensamenöl.*
Italian—*Olio di cotogno.*

The seeds of the quince, *Cydonia vulgaris,* Pers. (cultivated in Asia and Europe), contain about 15 per cent of a fatty oil of yellow colour, and of a pleasant odour faintly resembling that of almond oil.[1] The specimen examined by *Hermann* yielded 95·2 per cent of insoluble acids + unsaponifiable, and had the acid value 31·7.

The oil is stated to contain a liquid hydroxy acid, $C_{17}H_{32}(OH)CO_2H$, the dibromide of which melts at 108° C. (Vol. I. p. 569). The solid acids contain myristic acid and another solid acid not yet identified.

Physical and Chemical Characteristics of Quince Oil

Specific Gravity.	Solidifying Point.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index.	Maumené Test.
At 15° C.	°C.	Mgrms KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Butyro-refractometer. "Degrees."	°O.
0·922	−11 to −13 [2]	181·75 187·7 [2]	113 120·2 [2]	0·5	68·5 (at 25° C.)	73 [2]

[1] R. Hermann, *Arch. d. Pharm.,* 1899, 237, 358.
[2] Fabris and Settimj. *Atti del VI. Congresso internaz.,* Roma, 1907, vol. v. 751.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.	Solidifying Point.	Melting Point.	Iodine Value.
Per cent.	° C.	° C.	Per cent.
95·5	26·27	33·34	121·6
			Liquid Fatty Acids [1]
			132·1

CHERRY KERNEL OIL

French—*Huile de cerisier*.   German—*Kirschkernöl*.
Italian—*Olio di ciliegie*.

For tables of characteristics see p. 279.

The characteristics given in the tables refer to extracted oil.

Cherry kernel oil is obtained from the kernels of the cherry (*Prunus cerasus*, L.).   The kernels contain 35-36 per cent of oil.   In its fresh state the oil has a golden-yellow colour and a faint odour of almonds ; this odour is lost when the oil becomes rancid.

With nitric acid of specific gravity 1·4 cherry kernel oil becomes dark reddish brown ; with *Bieber's* reagent (p. 291) a brown colouration is obtained.

De Negri and Fabris found a notable quantity of hydrocyanic acid in the extracted oil.

In South Germany (Wurtemberg) the " cold-drawn " oil is used for edible purposes.   The oil expressed at a higher temperature serves as a burning oil, and also for soap-making.   Since cherry kernel oil easily turns rancid, it is not employed as an adulterant of almond oil.

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[1] The proportion of liquid fatty acids was 77·3 per cent.

[TABLE

Physical and Chemical Characteristics of Cherry Kernel Oil

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Maumené Test	
At 15° C.	Observer.	°C.	Observer.	Mgrms KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0 9235-0·9238	De Negri and Fabris	−19 to −20	De Negri and Fabris	194·8-195	De Negri and Fabris	110·8-110·9	De Negri and Fabris	45	De Negri and Fabris
0·9285	Micko			193·4	Micko	114·8	Micko		
						113 2[1]	Tortelli and Ruggeri		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Liquid Fatty Acids.	
° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.		Observer.
15-18	De Negri and Fabris	19-21	De Negri and Fabris	189	Micko	296·2	Micko	114·3	De Negri and Fabris	124·7	Tortelli and Ruggeri
...	...	16-20·6[2]	Micko	...	...	...	...	104·3	Micko		

[1] Cold-pressed oil.　　[2] Determined by the capillary tube method.

CHERRY LAUREL OIL [1]

French—*Huile de laurier cerise.*   German—*Kirschlorbeeröl.*
Italian—*Olio di lauroceraso.*

This oil has been extracted from the kernels of the cherry laurel, *Prunus laurocerasus*, L., a tree indigenous to Persia and the Caucasus, and cultivated in Italy since the sixteenth century.

Cherry laurel oil has a golden-yellow colour ; its odour resembles that of bitter almonds. Like the preceding oil it contains appreciable quantities of hydrocyanic acid.

Physical and Chemical Characteristics of Cherry Laurel Oil

Specific Gravity.	Solidifying Point.	Saponific. Value.	Iodine Value.	Maumené Test.
At 15° C.	° C.	Mgrms. KOH.	Per cent.	° C.
0·9230	− 19 to − 20	194	108 9	44·5

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.
° C.	° C.	Per cent.
17-15	20-22	112·1

APRICOT KERNEL OIL

French—*Huile d'abricotier.*   German—*Aprikosenkernol.*
Italian—*Olio di albicocche (Olio di armelline).*

For tables of characteristics see p. 281.

Apricot kernel oil is obtained from apricot kernels (*Prunus armeniaca*, L.), which contain from 40 to 45 per cent of oil.

The freshly expressed oil is almost colourless ; on keeping it turns yellow.

With nitric acid, spec. grav. 1·4, apricot kernel oil assumes an orange colour. With *Bieber's* reagent (p. 291) a peach-blossom colour is obtained, which is so characteristic of the oil, that apricot kernel oil can be thereby identified. This colour reaction also leads to the detection of apricot kernel oil in almond oil if considerable proportions have been used for adulteration.

[1] De Negri and Fabris, *Ann. d. Lab. Chim. delle Gabelle*, 1891, 173

Physical and Chemical Characteristics of Apricot Kernel Oil

	Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Butyro-refractometer.		
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent	Observer.	°C.	Observer.	At °C	"De-grees"	Observer.
15	0 9204	Maben	−20	Maben	192.2. 192·9	De Negri and Fabris	101	De Negri and Fabris	42·5	De Negri and Fabris	25	65·6	Beckurts and Seiler
15·5 (water at 15·5 = 1)	0·9193 1	Crossley and Le Sueur			193 11	Micko	108	Micko			40	57·51	Crossley and Le Sueur
	0·9172 5 0·9200 4	Lewko-witsch			1881	Crossley and Le Sueur	96·02	Crossley and Le Sueur			40	58 0 4	Lewko-witsch
90	0·901–0·9015	Dieterich			198 25 190·3. 192 1 4	Lewko-witsch ,,	104·2. 104·3	Tortelli and Ruggeri Wijs			40 50	57·05 52·25	,, Dieterich
							100 1 4 107·4. 108·7 4 107·9	Lewko-witsch ,,			20	1·4712	Harvey
15·5 (water at 15 = 5)	0·9198	Ross and Race			192·4	Ross and Race	101 4	Ross and Race			40	57·5	Ross and Race

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Mole-cular Weight.		Iodine Value.		Refractive Index. Butyro-refractometer.		
Per cent.	Observer.	At °C.	Observer.	°C.	Ob-server.	°C.	Observer.	Mgrms. KOH.	Ob-server		Ob-server.	Per cent.	Observer.	At °C.	"De-grees	Observer.
95·40 1	Crossley and Le Sueur	15	Dieterich	0	Hubl	4·5 2 3 } 3 5 }	Hubl De Negri and Fabris	194	Micko	288·6	Micko	103 8	De Negri and Fabris	25 40 50	56·3 56·0 41·3	Dieterich ,, ,,
		90	0·8875			13·4· 18 2	Micko	199·8	Ross and Race			102·6 99 4 103·4	Micko Dieterich Ross and Race	25	59	Ross and Race
												Iodine Value Liquid Fatty Acids.				
												111·1· 111·8 3 }	Tortelli and Ruggeri			

1 Oil from the Punjab.   2 Determined in a capillary tube.   3 Cold-pressed oil, eighteen months old.   4 Californian oil.   5 Mogador oil.

The red colouration with *Bieber's* reagent is given by the apricot kernel oil even after being subjected to steam distillation for some hours ; the residue gave the reaction strongly, but not so the distillate. Even after keeping for a year the colour reaction was still distinctly obtained.

The deep red colouration obtained on shaking the oil with an ethereal solution of phloroglucinol (one-tenth per cent solution) is not so characteristic of the oil as the colour test with *Bieber's* reagent, since some almond oils (see p. 291) give the same colour reaction.[1] It should also be noted that the colour reaction is much stronger in the case of fresh oils than with samples that have been kept for half a year and longer.

A specimen of pressed oil obtained from *Prunus armeniaca*, L., examined by *Uyeno*,[2] was light yellow in colour and had the following characteristics :—

Oil—

Specific gravity at 15° C.	.	.	.	0 9180
Solidifying point ° C.	.	.	.	below 11
Saponification value ° C.	.	.	.	178·3
Iodine value	.	.	.	105·2
Refractive index at 20° C.	.	.	.	1·4691

Fatty Acids—

Insoluble acids + unsaponifiable .	.	.	95·74 per cent
Specific gravity at 15° C.	.	.	.	0 9021
Neutralisation value	.	.	.	193·5
Mean molecular weight .	.	.	.	289·8
Iodine value	.	.	.	108·1
Refractive index at 20° C.	.	.	1·4626

Neither hexa- nor tetra-bromides could be obtained.

The distillation of the mixed fatty acids at 40 mm. pressure gave the following result (*Ross and Race*) :—

Fraction.	Butyro-refracto-meter " Degrees."	Iodine Value.	Neutralisation Value.
	(25° C.)		
1	46·0	85·2	203·7
2	47·0	87·1	..
3	49·0	89·6	..
4	49·5	90·3	..
5	52·0	93·1	..
6	57·0	97·5	..
Residue	86·5	129·6	193·7

Apricot kernel oil is used as an edible oil ; in perfumery it is employed for adulterating or wholly substituting almond oil. Apricot kernel oil forms an important article of commerce. The commercial " almond oil, French," is practically pure apricot kernel oil, or a mixture

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[1] Lewkowitsch, *Analyst*, 1904, 106.
[2] *Journ. Chem. Ind. Tokyo*, xvi. 185.

of apricot kernel and peach kernel oils (cp. p. 288). The French apricot kernel oil is obtained from sweet kernels; the oil obtained from Japanese bitter kernels (which are imported) is not so pleasant in taste.[1]

PLUM KERNEL OIL

French—*Huile de prunier.* German—*Pflaumenkernol.*
Italian—*Olio di susino, olio di prugne.*

For tables of characteristics see p. 284.

The characteristics given in the tables refer both to expressed and extracted oils.

Plum kernel oil is obtained from the kernels of plums (*Prunus domestica*, L., and *Prunus damascœna*, L.). The oil is light yellow in colour, and possesses an agreeable, mild, almond-like taste. *Fabris and Settimj* [2] obtained by extraction with petroleum ether 25 per cent of an oil yielding 70 per cent of liquid fatty acids.

With nitric acid, of specific gravity 1·4, plum kernel oil gives an orange colour (like apricot kernel oil). With *Bieber's* reagent, consisting of equal parts (by weight) of concentrated sulphuric acid fuming nitric acid, and water, a pink colouration is obtained.

The sample examined by *Micko* was comparatively fresh (acid value 0·55).

The oil is chiefly used to adulterate almond oil.

[1] Cp. L. Rosenthaler and W. Schaeffer, *Pharm. Zentralbl.*, 1911 (52), 507.
[2] *Atti del VI. Congresso, etc.*, Roma, 1907, vol. v. 759.

Physical and Chemical Characteristics of Plum Kernel Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Butyro-refractometer "Degrees."	
At °C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At 25° C.	Observer.
15	0·91949 De Negri and Fabris	−5 to −6	De Negri and Fabris	191·48	De Negri and Fabris	100·4	De Negri and Fabris	44·5-45	De Negri and Fabris	63·1	F. and S.
	0·9160 Micko[1]	−10	Fabris and Settimj	191·55	Micko	100·2	Micko				
				189·1	F. and S.	93·3[2]	Tortelli and Ruggeri				
						91·2	F. and S.				

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
96·2	Fabris and Settimj	15-18	De Negri and Fabris	20-22	De Negri and Fabris	200·47	Micko	279·3	Micko	102	De Negri and Fabris
		12-18	F. and S.	12·14·	Micko		...		...	104·2	Micko
				18·1[2]						95·7	F. and S.
										Liquid Fatty Acids.	
										98·6[3]	Tortelli and Ruggeri
										102·2	F. and S.

[1] *Journ. Soc. Chem. Ind.*, 1893, 935.   [2] Determined in a capillary tube   [3] Cold-pressed oil, eighteen months old.

PEACH KERNEL OIL

French—*Huile de pêcher.*   German—*Pfirsichkernöl.*
Italian—*Olio di pesche, Olio di pesco.*

For table of characteristics see p. 286.

Peach kernel oil (peach oil) is obtained from the kernels of the peach (*Prunus persica*, Sieb. et Zucc.) which contain 32-35 per cent of a pale yellow oil, resembling almond oil very closely. *Dieterich* states that the freshly expressed oil—of which he obtained 10-12 per cent from the kernels—smells slightly of hydrocyanic acid.[1] With nitric acid of the specific gravity 1·4, peach kernel oil becomes first yellowish-brown, afterwards dirty orange. With *Bieber's* reagent it remains unchanged at first,[2] then after about half-an-hour's standing becomes slightly pink, the pink colour being less strongly marked than is the case with apricot kernel oil. In the phloroglucinol test (see p. 291) peach kernel oil, like apricot kernel oil, gives a red colouration.

Klamroth[3] states that the solid portion of the unsaponifiable matter in peach kernel oil consists of sitosterol absorbing two atoms of bromine and is free from stigmasterol.

This oil is chiefly used for adulteration, or for substitution, of almond oil. The commercial " almond oil, French," is frequently a mixture of peach kernel oil with apricot kernel oil (cp. p. 288).

The oil is also sold under the name " Oleum amygdalæ persicæ," this name being based on the fact that the common peach was described in Gray's *Supplement to the Pharmacopœia* as *Amygdalus persica*, L.

Peach kernel oil is adulterated in its turn with poppy seed oil; in some cases commercial " peach kernel oil " was found to be hazel nut oil (*Bennett*[4]).

The seeds from *Prunus brigantiaca*, Vill., grown in the south-east of France, furnish on expression, the commercial " huile de marmotte."

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[1] This is confirmed by Fabris and Settimj. The oil obtained by these observers gave 84·5 per cent of liquid fatty acids.
[2] Lewkowitsch, *Analyst*, 1904, 106.   [3] *Inaug. Dissert.*, Munich, 1911.
[4] *Chemist and Druggist*, 1908, 89, 981.

Physical and Chemical Characteristics of Peach Kernel Oil

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Maumené Test		Refractive Index					
										Butyro-refractometer			Oleo-refractometer		
At °C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At °C.	"Degrees."	Observer.	"Degrees."	At °C	Observer.
15	De Negri and Fabris	Below −20	Maben	189·1	Maben	92·5–93·5	De Negri and Fabris	42·43	De Negri and Fabris	25	67·21	Dieterich	+7·5 to +11·5	22	Pearmain
15	Micko			192·5	De Negri and Fabris	99·7	Micko			,,	65·72	,,			
15·5	Lewkowitsch			191·1	Micko	109·71	Dieterich			,,	66·1	Beckurts and Seiler			
90	Dieterich			191·4	Lewkowitsch	98·62	,,			40	66·5	Mansfeld			
						94·84	Tortelli and Ruggeri			,,	58·51	Dieterich			
						110·1	Wijs			,,	57·02				
						95·24	Lewkowitsch			,,	57·5	Lewkowitsch			
										50	52·21	,,			
										,,	51·52	Dieterich			

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
94·0	Fabris and Settimj	Titer Test.	Lewkowitsch	3–5	De Negri and Fabris	209·9	Micko	278·8	Micko	94·1	N. and F.
		18–13·5		10–18·9	Micko	205·0	Lewkowitsch	…	…	101·9	Micko
										98·5	F. and S.
								Liquid Fatty Acids.			
										101·9	Tortelli and Ruggeri
										104·1	F. and S.

¹ Freshly prepared oil.   ² Old oil.   ³ Cold-pressed oil, eighteen months old.

ALMOND OIL

French—*Huile d'amande.* German—*Mandelol.*
Italian—*Olio di mandorle.*

For tables of characteristics see pp. 289, 290.

Almond oil is obtained from the seeds of *Prunus amygdalus*, Stokes (*Amygdalus communis*, L.). The commercial oil is expressed [or extracted] chiefly from bitter almonds, the seeds of *Prunus amygdalus*, var. *amara*. Bitter almonds contain amygdalin, and a ferment (emulsion) which, acting on the amygdalin, gives rise to the formation of benzaldehyde, glucose, and hydrocyanic acid.[1] Hence the press-cakes obtained in the preparation of almond oil find a profitable outlet in the manufacture of genuine " ethereal bitter almond oil " by triturating the meal with water.

The sweet almonds (from *Prunus amygdalus*, var. *dulcis*) are but rarely used alone for the preparation of almond oil. Mogador bitter almonds, which are largely used in this country for the manufacture of almond oil, are always more or less mixed with sweet almonds. The meal from sweet almonds is used in confectionery and for some toilet preparations.

The oils obtained from both varieties are practically identical, so that no definite difference can be established by chemical means ; this will be seen by a glance at the accompanying table. Nor can a definite botanical difference be established between the two varieties *amara* and *dulcis*. The principal countries supplying almonds are, Morocco, the Canary Islands, Portugal, Spain, France, Italy, Sicily, Syria, and Persia.

Sweet almonds yield from 44 to 55 per cent of oil, whereas bitter almonds may yield as little as 20 per cent of oil. On an average bitter almonds yield from 38 to 45 per cent of oil.

Almond oil contains, according to *Gusserow*, no stearic acid ; this is confirmed by *Hehner and Mitchell*.[2] The almond oil glycerides consist chiefly of olein ; the high iodine value points, however, to the presence of fatty acids less saturated than oleic. Indeed, *Farnsteiner* isolated from the mixed fatty acids linolic tetrabromide corresponding to 5·79 per cent of linolic acid.

The distillation of the mixed fatty acids at 40 mm. pressure gave the following results (*Ross and Race* [3]) :

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[1] Cp. K. Feist, *Arch. d. Pharm.*, 1908, 246. S. J. M. Auld, *Proc. Chem. Soc.*, 1908, 97. With regard to the occurrence of arsenic in almonds cp. F. Jadin and A. Anstruc, *Compt. rend.*, 1912, 893.

[2] *Analyst*, 1896, 328.

[3] *Analyst*, 1911, 264.

Fraction.	Butyro-refracto-meter Degrees. (25 ° C.)	Iodine Value.	Neutralisation Value.
1	44·0	82·9	205·1
2	45·0	84·7	..
3	47·0	88·0	..
4	48·5	89·9	..
5	51·0	91·2	..
6	55·5	96·7	..
Residue	82·0	119·3	194·6

Contrary to older statements, almond oil does not easily turn rancid. A number of genuine almond oils, 12 to 18 months old, examined in my laboratory, had acid values varying from 0·79 to 5·1 (see table, p. 292).

Almond oil is largely used in pharmaceutical practice, hence the pharmacopœia of each country prescribes certain reactions for identification. Most of these, such as the specific gravity test and the elaïdin test, are of very little use for this purpose. Of greater importance is the determination of the melting point of the mixed fatty acids, almond oil being characterised by a low melting point of its mixed fatty acids. According to the German Pharmacopœia the mixed fatty acids of pure almond oil should remain liquid at 15° C. for an indefinite length of time ; mixed with an equal volume of alcohol they should give a clear solution at 15° C., and not become turbid on adding twice the volume of alcohol. *Olive, sesamé, arachis,* and *cotton seed oils* may thus be detected. *Apricot* or *peach kernel oils* will, however, escape detection.

Older statements that almond oil is adulterated with the following oils :—poppy seed, walnut, cotton seed, sesamé, arachis, olive, lard oils, hardly hold good to-day. It need, therefore, only be briefly pointed out that poppy seed, walnut, cotton seed, and also sesamé oils would be detected by high iodine values. Confirmatory tests to be applied would be :—in the case of cotton seed oil, the *Halphen* colour test, and the melting point of the mixed fatty acids ; and in the case of sesamé oil, the *Baudouin* colour reaction. Arachis oil would be identified by the isolation and determination of arachidic acid ; olive oil by the high melting point of the fatty acids, and the solidifying point of the oil itself ; lard oil by the phytosteryl acetate test.

The chief adulterants of almond oil are apricot kernel oil and peach kernel oil. The latter oils are used to such an extent, that frequently they are entirely substituted for almond oil ; indeed " foreign " almond oil, or " oil of sweet almonds, French," *Oleum Amygdalarum Gallicum*. is nothing else but a mixture of apricot kernel oil and peach kernel oil. Genuine almond oil is sold in commerce under the name " almond oil, English." Pure almond oil may be differentiated from apricot and peach kernel oils by its lower iodine value, so that an almond oil having an iodine value exceeding 105 must be looked upon with suspicion. The differentiation of almond oil from these two oils by means of the colour tests described below will not lead to decisive results in every case, owing to the different behaviour of almond oils from various sources.

Physical and Chemical Characteristics of Almond Oil

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value	
At ° C.	Observer	° C.	Observer	Mgrms. KOH.	Observer	Per cent.	Observer
12	0·9168 [1]	− 10	Girard	195·4	Valenta	97·5	Del Torre
„	0·9154 [2]	− 21	Maben	190·9	Dieterich	98·4 [2]	Moore
15	0·9180			190·5–191·2 [2]	De Negri and Fabris	93–95·4 [2]	De Negri and Fabris
„	0·9190			189·5–191·7 [1]	„	94·1–96·5 [1]	„
„	0·9190–0·9195 [2]						
„	0·9175–0·9195 [1]					95·8 [2]	Tortelli and Ruggeri
„	0·9177–0·9185					95·8–101·26	Allen and Brewis
15·5	0·9186					98·5–100·2 [2]	Lewkowitsch
„	0·9178–0·9183						

De Negri and Fabris (Specific Gravity); Allen and Brewis; Tolman and Munson; Lewkowitsch

[1] From bitter almonds.   [2] From sweet almonds.

Refractive Index.		
At ° C.		Observer.
15·5	1·4728	Tolman and Munson
20	1·4705	Harvey
60	1·4555	Thoerner

Oleo-refractometer.	
"Degrees."	Observer.
+ 6	Jean
+ 7	Bruyn and van Leent
+ 8 to + 10·5 at 22° C.	Pearmain

Butyro-refractometer.		
At ° C.	"Degrees."	Observer.
15·5	70·9	Tolman and Munson
25	64·8	Beckurts and Seiler
	64·0	Dieterich

Thermal Tests.		
Maumené Test.		
° C.		Observer.
51·52 [2]		De Negri and Fabris [3]
51·53 [1]		„

Heat of Bromination.	
° C.	Observer.
17·6	Hehner and Mitchell
20·25	Bromwell and J. L. Meyer
20·6–21	Allen and Brewis

[1] From bitter almonds.   [2] From sweet almonds.   [3] Jeans' thermometer.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point		Melting Point		Neutralisation Value		Iodine Value		Refractive Index	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
Titer Test.		14	Hübl	204	Thoerner	93·5-95·5 [2]	De Negri and Fabris	1·4461	Thoerner
9·5-10·1 [2]	Lewkowitsch	13-14 [1,2]	De Negri and Fabris			94·1-96·5 [1]	,,		
11·3-11·8 [1]	,,					Liquid Fatty Acids.			
						101·7 [2]	Tortelli and Ruggeri		

[1] From bitter almonds   [2] From sweet almonds.

The close relationship in which apricot kernel and peach kernel oils stand to almond oil renders their detection in an adulterated almond oil a very difficult problem, which cannot be solved with certainty in the present state of our knowledge, since most of the physical and chemical characteristics, including the iodine value, fail to reveal the presence of the kernel oils.

In doubtful cases recourse may be had to the following colour reactions, which should, however, be looked upon as confirmatory tests only, and as more suitable for differentiating peach kernel and apricot kernel oils severally from almond oils, than for detecting the former oils when admixed with almond oil.

Nitric Acid Test.—Almond oil, shaken with nitric acid of specific gravity 1·4, remains colourless, or becomes only slightly yellow, whereas apricot kernel oil assumes an orange yellow colour, and peach kernel oil becomes yellowish brown, subsequently passing into a dirty-orange colour.

Bieber's Test is carried out by agitating five volumes of oil with one volume of a mixture consisting of equal parts (by weight) of concentrated sulphuric acid, fuming nitric acid, and water. Pure almond oil does not change its colour, whereas apricot kernel oil gives a pink (peach-blossom) colour, and peach kernel a faint pink colouration after standing for some little time. I find that it is necessary to prepare *Bieber's* reagent afresh for each test; it should also be noted that the colour reaction is much more distinct in the case of freshly expressed oil than in the case of a sample which has been kept for half a year and longer (*Lewkowitsch*).

Whereas it is thus possible to differentiate broadly almond oil from apricot and peach kernel oils, it would be hazardous to pronounce adulteration on the strength of these colour tests alone. Mixtures of almond oil and apricot kernel oil containing equal parts of each oil still show distinctly the colour reaction of the latter, but mixtures containing 25 per cent of apricot kernel oil can no longer be detected with certainty (*Lewkowitsch* [1]).

Recently, a $\frac{1}{10}$ th per cent solution of phloroglucinol in ether, applied in the presence of nitric acid, has been proposed to detect apricot kernel and peach kernel oils.[2] Nitric acid of specific gravity 1·45 gives, in my experience, better results than the acid of 1·42 specific gravity recommended by *Chwolles*. Undoubtedly apricot kernel oil and peach kernel oil give distinct deep red colourations with the reagent, in contradistinction to some almond oils; yet other specimens of genuine almond oils tested in my laboratory (see table, p. 292) show the same reaction more or less strongly. This test must, therefore, be employed with even greater circumspection than *Bieber's* test.

In the following table I have collated a number of tests carried out with genuine almond oils. A comparison of these numbers with those given for apricot and peach kernel oils, will, in doubtful cases, render some assistance to the analyst.

[1] *Analyst*, 1904, 106.
[2] Chwolles, *Pharm. Zeit.*, 1903, 109. The reagent was first proposed by Kreis. Cp. Fahrion, *Zeitschr. f. angew. Chem.*, 1904, 869.

Characteristics of some Almond and Allied Oils (Lewkowitsch)

Description of Oil	Specific Gravity	Saponification Value	Iodine Value	Butyro-refractometer at 40° C.	Acid Value	Fatty Acids		Colour Reactions	
						Neutralisation Value	Saponification Value	Bieber's Test	Phloroglucinol Test
				"Degrees."					
Almond Oils, expressed from—									
1. Valencia Sweets	0·91995		99·4	57·5	5·16	207·8	207·6	Colourless	No colouration
2. Blanched Valencia Sweets	0·9182	191·7	103·6	57·5	2·9	196·4	201·7	,,	No crimson colouration
3. Sicily Sweets	0·9178	183·3	100·3	57·0	0·79	198·8	202·2	,,	,,
4. Mazagan Bitters	0·9180	188·6	102·5	56·5	3·1	196·8	203·1	,,	Slightly crimson
5. Small Indian Almonds	0·91907	189·2	96·65	57·0	2·9	195·8	200·7	,,	,,
6. Mogador Bitters	0·9183	194·98	104·2	57·0	1·3	197·1	203·2	,,	No crimson colouration
7. Peach Kernel Oil	0·9193	191·4	95·24	57·5	3·0	196·8	205·0	Colourless at first, then pink	Deep crimson
8. Apricot ,, ,,	0·9200	192·4	107·4	58·0	2·3	198·0	202·0	Pink colouration	,,
9. Kernels ,, ,, from Mogador	0·9172	198·2	107·9	57·0	2·8	191·0	200·7	Slightly pink	Less deep crimson than 8
10. Californian Apricot Kernel Oil	0·92026	190·3	108·7	58·0	1·2	197·8	202·8	Very slightly pink	,,

The following refractive indices for different rays, have been deter-, mined by *Ross*;[1] unfortunately, these numbers do not furnish a means of differentiating almond oil from the related oils.

Refractive Indices at 20 Degrees Centigrade (Ross)

Oil	D	C	F	G
No. 1	1·4715	1·4688	1·4780	1·4835
,, 2	1·4715	1·4688	1·4780	1·4836
,, 3	1·4711	1·4685	1·4777	1·4833
,, 4	1·4712	1·4686	1·4778	1·4834
,, 5	1·4710	1·4685	1·4777	1·4833
,, 6	1·4714	1·4688	1·4780	1·4835
,, 7	1·4710	1·4685	1·4776	1·4832
,, 8	1·4717	1·4692	1·4784	1·4839
,, 9	1·4715	1·4690	1·4782	1·4837
,, 10	1·4725	1·4700	1·4792	1·4847

Almond oil is too expensive to admit of any other use than ... pharmaceutical practice and for high-class toilet soap. Statements in the technical literature and even in patent specifications as to the employment of almond oil in the manufacture of oil varnishes must therefore be accepted with the greatest reserve. Although its price would not militate against its use as a lubricating oil for fine machinery, it cannot be recommended for this purpose.

WHEAT-MEAL OIL

French—*Huile de farine de froment.* German—*Weizenmehlol.*
Italian—*Olio di farina di frumento.*

This oil is extracted from wheat flour,[2] and must not be confounded with wheat oil. The proportion of fat in ten samples of wheat meal examined by *Plücker* [3] varied from 0·99 to 1·63 per cent.

Physical and Chemical Characteristics of Wheat-Meal Oil

Specific Gravity at 100° (water 15° C. = 1).	Saponifica- tion Value.	Reichert- Meissl Value.	Iodine Value.	Refractive Index At 25° C.	Observer.
0·9068	166·5 (?)	2·8	101·5	1·4851	Spaeth
				Butyro- refracto- meter. "Degrees."	
...	182·8	...	...	92 ..	De Negri and Fabris
...	...	2·95-4·95 [4]	96·1-112·5 [4]	92	Plücker

[1] *Analyst*, 1904, 106.
[2] Spaeth, *Analyst*, 1896, 234.   Cp. *Chem. Revue*, 1904, 127.
[3] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907 (xiv.), 751.
[4] Minimum and maximum numbers of ten samples.

SANGUINELLA [1] OIL, DOGWOOD OIL, CORNEL OIL

French—*Huile de cornouiller.*   German—*Hartriegelöl.*
Italian—*Olio di sanguinella.*

The seeds of the dogwood (cornel tree), *Cornus sanguinea*, L., contain 55 per cent of a greenish-yellow oil. *Grimaldi* gives a colour reaction for the detection of cornel oil in olive oil; for the description of the colour test the reader is referred to the original.[2] Sanguinella oil is used in Italy as a burning oil, and for soapmaking.

Physical and Chemical Characteristics of Sanguinella Oil

Specific Gravity at 15° C.	Solidifying Point. ° C.	Saponific. Value. Mgrms.KOH.	Iodine Value. Per cent.	Maumené Test. C.	Butyro-refracto-meter.	Observer.
0·921	− 15	192·11	100·8	52	..	De Negri and Fabris
0·921-0·9225	− 12 to − 15	192·192·5	100·101	53·54 [3]	62·63 "Degrees" at 25° C.	Grimaldi

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point. ° C.	Melting Point. ° C.	Neutralisation Value Mgrms. KOH.	Iodine Value. Per cent.	Observer.
31·29	34·37	195·1	102·75	N. and F.

ACORN OIL [4]

French—*Huile de gland.* German—*Eicheckernol*; *Eichelöl.*
Italian—*Olio di ghiande.*

This oil is obtained by extracting the fruit of *Quercus agrifolia.* It is a deep brown fluorescent oil, from which after long standing some "stearine" separates.

Physical and Chemical Constants of Acorn Oil

Specific Gravity at 15° C.	Solidifying Point. ° C.	Saponification Value.	Iodine Value.	Maumené Test. ° C.	Refractive Index.
0 9162	10	199·3	100·7	60 [5]	1·4731

The melting point of the fatty acids is 25° C.

[1] De Negri and Fabris, *Annali, etc.*, 181.
[2] *Staz. sperim. agrar. ital.*, 1911 (44), 291. [3] In Tortelli's thermolcometer.
[4] Blasdale, *Journ. Soc. Chem. Ind.*, 1896, 206. [5] Jean's thermelæometer.

CALIFORNIAN NUTMEG OIL [1]

French—*Huile de noix de Californie.*   German—*Kalifornisches Muskatöl.*   Italian—*Olio di noci di California.*

Californian nutmeg oil is obtained from the fruit of *Tumion californicum.*

Physical and Chemical Characteristics of Californian Nutmeg Oil

Specific Gravity at 15° C.	Saponific. Value. Mgrms. KOH.	Iodine Value. Per cent.	Maumené Test. ° C.	Refractive Index.
0·9072	191 3	94·7	77 [2]	1·4766

The melting point of the fatty acids is 19° C.

OWALA OIL,[3] FULLA PANZA OIL,[4] ATTA SEED OIL.

French—*Huile d'owala.*   German—*Owala Öl.* Italian—*Olio di owala.*

For tables of characteristics see p. 296.

This oil is obtained from the seeds [4] of *Pentaclethra macrophylla,* Benth., a *Mimosea* growing on the West Coast of Africa.[5]   The seeds, termed by the natives " owala " (*Gaboon*), " opachala " (*Sousouland*), or " atta beans," " fai beans " have the form of a mussel ; they consist of 20·6 per cent of husks and 79·4 per cent of kernels.   The weight of the whole seeds varies from 8 to 20 grms.   The seeds yield 30·4 per cent, and the kernels 41·6 per cent of oil.

The oil (extracted with ether) has a faint yellowish colour, pleasant taste, and aromatic odour.

A specimen of oil prepared by the natives and supplied to the author (through reliable sources) yielded on examination (by the lead-salt-ether method) in two experiments, 24·7-28·60 per cent of liquid acids and 70·2-74·8 per cent of solid acids.   The mean molecular weights of the acids were respectively 320 and 346.   From the solid acids an acid melting at 78-79° C., and crystallising in white laminæ, was isolated.   This oil contained 2·74 per cent of unsaponifiable matter. Oil prepared in the author's laboratory from the seeds by extraction with ether yielded 2·50 per cent of unsaponifiable matter (*Wedemeyer* 0·54 per cent, *Grimme* 3·2 per cent).

[1] Blasdale, *Journ. Soc. Chem. Ind.,* 1896, 206.   [2] By Jean's thermelæometer.
[3] Wedemeyer, *Chem. Rev.,* 1906, 210 ; *Bull. Imp. Inst.,* 1907, 10.
[4] The native name for the seeds and the oil in the Congo is Fulla Panza seeds and Fulla Panza oil.   In Angola the seeds are known as "Nulla Panza."
[5] E. Drabble, *Quart. Journ. Inst. of Comm. Research* (Liverpool University), 1907, April ; Cl. Grimme, *Chem. Rev.,* 1910, 157, cp. "Dika Oil."

Physical and Chemical Characteristics of Ocuba Oil

	°C.	Specific Gravity.	Solidifying Point °C.	Melting Point °C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Maumené Test. °C.	Refractive Index. 40° C.	Butyro-refractometer. "Degrees." 40° C.	Observer.
Native oil	25	0·9119	4 "Stearine" separates at 18° to 19°; becomes a buttery mass at 8°.	...	186	99·3	100°	1·4654	...	Wedemeyer
	100 (water at 15° C.=1)	0·9036	8	...	...	94·3	...	...	...	Imperial Institute
	40			22·24·5	167·6				59·2	Spiegel[1]
Extracted oil	40 (water at 15° C.=1)	0·9041	15·5-20·6	...	169·3	98·4	...	...	...	Warburton[1]
	15 (water at 15° C.=1)	0·9259 (?)	5-7	...	203	85·7	...	1·4728 (30)	...	Grimme[2]

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable. Per cent.	Solidifying Point °C.	Melting Point °C.	Neutralisation Value. Mgrms. KOH.	Observer.
95·6	52·1	53·9 (capillary tube)	185·7	Wedemeyer
94·2	...	52·4	...	Imperial Institute
91·85	...	...	...	Grimme

[1] Determined in the author's laboratory. [2] *Chem. Rev.*, 1910, 158.

ARACHIS OIL, PEANUT OIL, EARTHNUT OIL, GROUND NUT OIL

French—*Huile d'arachide.*   German—*Arachisöl, Erdnussol.*
Italian—*Olio di arachide.*

For table of characteristics see pp. 307-309.

Arachis oil is obtained from the seeds of *Arachis hypogœa*, L. (*Leguminosœ*) known as earthnuts (" monkey nuts ").

The cultivation of the arachis plant dates back so far in history that its origin cannot be located with certainty ; but it is generally assumed that the home of the arachis nut is Brazil. *Arachis hypogœa* represents a cultivated variety derived from *A. prostrata*, Benth.[1]

The arachis plant is chiefly cultivated [2] in Japan, the East Indies, Burma, China, Indo-China, Java, Mozambique, the West Coast of Africa (latterly also in Togo [3] and Southern and Northern [4] Nigeria), Madagascar, Algeria, Egypt, Spain, Sicily, the United States of America (chiefly in Virginia,[5] Georgia, Tennessee, and North Carolina [6]), Mexico, Brazil, La Plata (especially in the provinces Salta Jujun, Tucuman, Santiago del Estero, Chaco, Formosa, Cordoba, and Santa Fé of the Argentine), and also in the following West Indian Islands : Jamaica, Trinidad, Grenada, Carriacou, St. Vincent, St. Lucien, Santa Lucia, Barbados, St. Kitts.   The East Indian and the West African nuts represent two distinct varieties.   The Indian (Bombay and Coromandel) and Mozambique earthnuts are usually decorticated before shipment to Europe.   As they undergo " heating " on the voyage, they cannot be used for the production of best edible oil, and are mainly worked up for soap oils.   The nuts from the Coromandel coast are wholly worked up for soap oil ; those from Bombay yield oil of somewhat better quality, which can be used as a lower quality of edible oil but is chiefly employed as lubricating oil, for oiling wool, etc.   The Mozambique nuts yield an edible oil of inferior quality, as only those seeds which are imported in their shells furnish the finest edible oils.   Less important in the world's commerce are the arachis nuts produced in Japan, Madagascar, Egypt, and Mexico.

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[1] Cp. Marcel Durant, *Bull. du Muséum d'histoire naturelle,* 1906 (5), 340 ; J. Adam, *L'Arachide ; culture, produits, commerce, etc.,* Paris, 1908.   Th. Fleury, *L'Arachide (principalement celle de la Sénégambie),* Bordeaux, Féret et fils, 1900.

[2] With regard to the diseases of the arachis plant cp. A. Zimmermann, *Der Pflanzer,* 1907, v. 125.

[3] The experiments made in Togo have up till now not led to satisfactory results.

[4] Cp. *Bull. Imp. Inst.,* 1910, 153.   A Chevalier, *Les Végétaux utiles de l'Afrique tropicale française,* vol. i. fascicules I-V.

[5] The Virginia nuts are stated to contain normally 0·015 per cent of boric acid. (*Chem. Zeit.,* 1909, 307).

[6] The cultivation of arachis nuts in the United States is being rapidly extended especially in the Southern part of Arkansas, the Eastern part of Texas, the Northern part of Louisiana, and the South of Mississippi.

The arachis nuts grown in the United States are almost exclusively worked up for edible oil. The home-grown seeds do not suffice for the demand, and therefore large quantities must be imported. Since decorticated nuts would be useless to the American oil manufacturer (owing to the changes they undergo during the voyage), nuts are imported exclusively in the shell from the West Coast of Africa. The largest arachis nuts are obtained from the plants cultivated in Fiji.

The chief producer of arachis nuts is Senegal. The quantities shipped to Europe are set out in the following table :—

[TABLE

Exports of Arachis Nuts in Shells from Senegal

Double (metric) hundredweights

From	1900* Total Exports	Chief Destinations		1901 Total Exports	Destinations	1902 Total Exports	Destinations	1903 Total Exports	Destinations	1904 Total Exports	Destinations	1905* Total Exports	Destinations
Rufisque et Cayor	1,063,457	France	814,021	893,502	608,832	715,016	478,492	867,192	588,732	730,279	440,361	561,267	379,599
		Holland	111,105		148,571		112,082		152,009		165,619		124,027
		Germany	76,691		83,640		108,735		103,489		77,462		45,998
		Belgium	28,388		38,886		14,430		41,470		45,666		7,107
		Denmark											...
Galam	3,620	France	3,620	280	230	4,000	4,000	2,250	2,250			9,290	9,290
		Holland											...
Petite-Côte	328,054	France	305,387	324,091	283,683	355,889	326,160	531,007	459,021	595,016	464,792	355,068	278,826
		Holland	8,870		21,044		21,729		52,416		77,652		56,639
		Belgium	5,593				...				34,951		19,657
		Denmark			...								...
Casamance	13,447	France	,551	11,050	9,696	27,337	27,836	76,723	72,999	32,369	28,225	33,282	33,087
		England and Colonies	3,036		1,354				11,162		4,148		195
		Germany											
Other regions	630	France	630	5,891	3,049	3	...	11,162	11,162	163	168	2,837	...
		England											...
		Gambia			...								
Total	1,409,208			1,234,524		1,102,245		1,488,424		1,377,832		961,745	

Exports of Arachis Nuts in Shells from Senegal (continued)

Double (metric) hundredweights

From		1906 Total Exports	1906 Chief Destinations	1907 Total Exports	1907 Destinations	1908 Total Exports	1908 Destinations	1909 Total Exports	1909 Destinations	1910 Total Exports	1910 Destinations
Rufisque et Cayor	Total	83,140,465		135,425,950		123,527,518		207,863,307		227,299,048	
	France		60,166,390		107,600,343		89,125,758		158,071,762		France 16,636,1
	Holland		14,778,785		17,292,060		29,098,175		28,897,235		England 490,9
	Germany		3,847,496		4,001,441		5,326,666		12,663,884		Germany 14,268,7
	Belgium		1,700,000		2,734,000		7,595,964		3,502,911		Holland 36,007,2
	Denmark		...		1,624,000						Belgium 2,972,6
	Austria										3,205,8
	Hungary										
	Portugal										2,020,0
	Gambia										1,827,25
	Other countries										1,240,00
Galam	Total	6,543,492		3,462,636		3,223,397		1,598,586			
	France		5,592,492		3,462,636		2,590,397		1,598,586		
	Holland						663,000				
Petite-Côte	Total	6,115,293		7,178,399							
	France		5,083,720		6,018,003						
	Holland		345,355		833,615						
	Belgium		736,218		326,651						
	Denmark		...								
Casamance	Total	4,566,549		7,786,461		8,144,632		2,436,664			
	France		784,785		5,853,389		6 574,910		11,448,070		
	England and Colonies		...		1,049,072		82,951				
	Germany		300,000				1,486,771		15,559		
Other regions	Total	89,000		598,500		9,214,177		2,436,664			
	France		...		598,500		7,242,900		2,436,664		
	England		...				616,130				
	Gambia		...								
Total		101,365,799		154,446,906		144,131,724		214,335,221			

The value of the arachis nuts exported from the Gambia Colony and Protectorate in 1906 was £278,065.

The value of the exports of arachis nuts from East India is given in the following table :—

Export of Groundnuts from East India to France and other Countries

Countries.	1899-1900.	1900-1.	1901-2.	1902-3.	1903-4.	1904-5.	1905-6.	1906-7.
	£	£	£	£	£	£	£	£
France	55,868	93,499	494,694	399,625	610,877	567,511	501,917	703,281
Other countries	10,667	16,421	30,254	77,569	147,063	77,668	77,129	133,703
Total	66,535	109,920	524,948	477,194	757,940	645,179	579,046	836,984

Countries.	1907-8.	1908-9.	1909-10.	1910-11.	1911-12.
	£	£	£	£	£
France	661,049	815,199	1,359,872	1,633,321	1,592,550
Other countries	124,864	85,170	179,632	377,165	494,030
Total	785,913	900,369	1,539,504	2,010,486	2,086,580

The chief centres of the arachis oil industry are Marseilles, Bordeaux, Dunkirk, Valencia, Trieste, and Delft.

The quantities of arachis nuts imported into France, and Marseilles in particular, are set out in the following table :—

Imports of Arachis Nuts into France and Marseilles

Kilograms

Year.	In Shells.		Decorticated.	
	France.	Marseilles.	France.	Marseilles.
1896	54,252,365	27,680,697	48,884,155	45,199,413
1897	61,440,732	30,414.186	6,959,204	6,753,230
1898	93,684,247	59,412,500	4,764,114	4,763,984
1899	94,495,450	60,685,291	11,786,721	7,232,671
1900	134,266,526	81,050,270	21,295,979	22,520,879
1901	120,408,208	72,092,808	58,132,221	54,486.709
1902	104,944,350	61,649,228	119,451,509	110,814,639
1903	146,888,425	94,116,177	100,339,519	86,223,015
1904	134,658,090	81,961,845	110,067,445	99,392,359
1905	102,900,986	57,106,499	100,746,178	97,092,561
1906	109,871,900	72,927,138	114,210,900	110,729,835
1907	163,241,200	120,550,102	117,404,000	109,230,215
1908	154,083,000	102,188,000	84,807,000	85,653,000
1909	219,208,000	155,056,000	160,140,000	170,012,000
1910	241,208,000	147,727,000	178,077,000	166,621,000
1911	216,770,000	148,838,000	178,379,000	202,274,000

It will be seen that Marseilles receives more than half the arachis nuts (both in shells and decorticated) exported from the West Coast of Africa. These nuts are classed according to their quality as follows :—

Rufisque, Cayor . . . ⎫
Sine . . . . ⎬1st quality
Nianing and Joal . . . ⎭
Saloum . . . ⎫
Gambia . . . ⎬2nd quality
Galam . . . ⎭
Casamanca . . . ⎫
Bissao . . . ⎬3rd quality
Boulam . . .
Rio-Nunez . . . ⎭

Imports of Arachis Nuts into Germany

Metric Tons

From	1908.	1909.	1910.	1911.	1912.
British West Africa .	..	..	..	1,597	4,619
German East Africa .	..	..	..	1,430	1,964
French West Africa .	..	..	..	17,368	21,758
Portuguese East Africa .	..	..	..	3,834	1,866
Portuguese West Africa .	..	..	..	2,882	2,791
India	..	..	..	30,249	25,820
China	..	..	..	7,699	6,995
French East Indies .	..	..	..	678	1,190
Dutch East Indies .	..	..	..	3,221	1,307
Total . . .	23,619	49,909	69,133	68,958	68,310

Imports into and Exports from Germany of Arachis Oil

Metric Tons

Imports			Exports		
From	1911.	1912.	To	1911.	1912.
France . . .	155	417	Belgium . . .	389	198
Holland . .	260	632	Denmark . .	2042	2969
			United Kingdom .	873	2230
			Holland . . .	1343	1881
			Norway . .	244	774
			Austria-Hungary .	150	258
			Sweden . . .	1307	1921
			Switzerland . .	643	412
			United States of America . .	38	955

The importance of the Dutch arachis nut trade is shown by the following table :—

Year.	Imports.	Exports.
	Metric Tons.	Metric Tons.
1901	21,634	6,312
1902	27,155	10,755
1903	32,948	13,000
1904	37,937	12,607
1905	26,660	6,318
1906	26,957	11,250
1907	27,296	9,367
1908	37,951	14,248
1909	51,761	20,556
1910	58,597	12,117
1911	47,581	12,762

The exports of earthnuts from Java in 1910 were 18,000 tons; in 1911, 25,000 tons; and in 1912, 11,400 tons.

Exports of Arachis Nuts from Gambia

	Tons.	£
1908	31,964	245,084
1909	53,644	323,231
1910	58,456	387,943
1911	47,931	437,472
1912	64,169	502,069

The following data are taken from actual results on a large scale in South of Europe oil mills. Arachis nuts in shells coming from

Rufisque, Saloum, Sine, Gambia—termed in the trade " haut de côte " —contain 35-36 per cent of oil; the kernels alone contain 50-51 per cent. On a large scale the nuts yield 28-30 per cent of shells and 31·5-32·5 per cent of oil, the press cakes retaining from 8 to 9 per cent of oil. Calculated on the kernels, they yield 44·5-45·5 per cent of oil.

The Casamanca nuts—termed in the trade " bas de côte "—contain 34-35 per cent of oil, and the kernels 50 per cent. On a large scale they yield 30-32 per cent of shells and 30·5-31·5 per cent of oil.

The decorticated Bombay and Coromandel [1] nuts contain 42 to 44 per cent of oil. On a large scale they yield 36 to 38 per cent of oil. Decorticated Mozambique nuts contain 46 to 48 per cent of oil, and yield on a large scale 40 to 42 per cent.

La Plata nuts yielded only 27·5-28 per cent of oil. This oil is, as a rule, paler than the oil from West African nuts.[2]

Arachis nuts harvested in the Cameroons seem to be the richest in content of oil. Nuts harvested in Lomie were found to contain 9·86 per cent of water and 65·7 per cent of fat calculated on dry kernels. The richness of the kernels as regards oil seems to depend on conditions of soil and cultivation; the more inland the nuts are harvested the better seems to be their condition.

The nuts are first shelled, if necessary, by special machinery, and the inner or red skin [3] which surrounds the kernel is removed as completely as possible by a blast of air, in a manner similar to that employed for cleaning wheat in flour mills. The husks are as a rule blown into the boiler-house to serve as fuel, or are ground and mixed with the arachis meal. The inner skins are added to the refuse meal, and are expressed with it. . The separated and cleaned kernels are then ground and subjected to hydraulic pressure. Since the kernels contain from 43 to 45 per cent of oil, expression of the oil is carried out in two stages (cp. Chap. XIII.). Frequently the meal is expressed three times. The first expression takes place at the ordinary temperature, the second at a temperature of 30° to 32° C., and the third at 50° to 55° C.

The " cold drawn oil " of the first expression is nearly colourless, and has a pleasant taste recalling the flavour of kidney beans. It is used as salad oil, and sold under the name " huile surfine " de Rufisque, Gambia, Sine, etc. The oil obtained by second expression also serves for edible purposes or for burning. The third quality, expressed at the highest temperature, is chiefly used for soap-making. This oil is somewhat thick and turbid, and must therefore be brightened by filtration.

A comparison of the specific gravities and iodine values of different arachis oils of first expression and second expression has been given by *Wijs*.[4] For edible purposes the oil is required to be almost water white; hence it is filtered over fuller's earth or charcoal (cp. Vol. III.

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[1] Decorticated coromandel nuts are bought in Marseilles only on condition that foreign matters do not exceed 3 per cent.

[2] J. Adam, *L'Arachide, etc.*, p. 88.

[3] These skins contain on an average 14 per cent of oil (C. S. Fuchs, *Chem. Zeit.*, 1911, 358).

[4] Wijs, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1903, 492.

Chap. XV. " Edible Oils "). It should be noted that arachis oil is usually pressed in the same establishment as sesamé oil, and since it is impossible to keep presses and press cloths separate for each kind of oil, commercial arachis oil contains a sufficient amount of sesamé oil to give the colour reaction of the latter faintly. Due regard should be paid to this fact in judging a commercial sample of arachis oil which gives a faint *Baudouin* reaction.[1]

The cakes serve as an excellent cattle food, as they contain the highest amount of proteins of all known oil cakes ; moreover, these proteins are more easily digested than those of other cakes. (With regard to the alleged toxic effect observed occasionally after feeding cattle with arachis cake, compare *Benecke*,[2] *Krüger*,[3] *Mooser*,[4] *Lewko-witsch*,[5] *Hefter*.[6]) The cakes from non-decorticated nuts contain 5·35 per cent of nitrogen and 0·9 per cent of phosphoric acid ; cakes from decorticated nuts contain 7·9 per cent of nitrogen and 1·35 per cent of phosphoric acid. The cakes from damaged or mouldy seeds serve as a valuable fertiliser in the South of France and in Italy (especially for early fruit).

On standing slightly above 0° C. arachis oil deposits a " stearine," which does not readily settle out as a crystalline mass. A number of experiments carried out by the author[7] show that even when crystals are once obtained, the very slight rise of temperature caused by handling the material suffices either to melt the crystalline mass, or to convert it into a gelatinous form, which withstands all attempts at filtering.

If the " stearine " has settled out by prolonged standing in the cold, an arachis oil less rich in solid glycerides can be drawn off leaving the " stearine " behind. A " margarine d'arachide " of the iodine value 79·4, melting point 21·5° C., represents a " stearine " so obtained on a large scale.[8]

Palmitic acid, stated by *Caldwell*[9] to occur in arachis oil, could not be detected by *Kreiling*.[10] *Gössmann* was the first to prove the presence of arachidic acid. *Kreiling* detected lignoceric acid, which can be separated from arachidic acid by means of alcohol (cp. below). The occurrence of stearic acid amongst the solid fatty acids was assumed by *Hehner and Mitchell*,[11] a specimen of oil examined by them having given 7 per cent of " stearic acid " crystals of the melting point 67° C. This " stearic " acid no doubt consisted chiefly of " arachidic " acid, of which arachis oil contains about 5 per cent. Indeed it has been shown by *Meyer and Beer*[12] to consist of a mixture of lignoceric and arachidic acids.

Gössmann and Scheven,[13] and also *Schröder*,[14] claim to have found

[1] Cp. also Fendler, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1903, 411.
[2] *Landw. Versuchsst.*, 34, 145.   [3] *Chem. Zeit.*, 1906, 999.
[4] *Landw. Versuchsst.*, 1904, 331.   [5] *Journ. Soc. Chem. Ind.*, 1908, 430.
[6] *Seifensieder Zeit.*, 1908, 1277.
[7] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1903, 592.
[8] Wijs, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1903, 492.
[9] *Liebig's Annal.*, 1857 (101), 97.   [10] *Berichte*, 1888, 880.
[11] *Analyst*, 1896, 328.   [12] *Monatsh. f. Chem.*, 1913, 1195.
[13] *Liebig's Annal.*, 1855 (94), 230.   [14] *Ibid.* 143, 22.

amongst the liquid fatty acids hypogæic acid (Vol. I. p. 176), whereas *Schoen*,[1] asserted that oleic acid is the only unsaturated acid in arachis oil. *Hazura's*[2] conjecture that hypogæic acid forms a constituent of the unsaturated glycerides in arachis oil is confirmed by the fact that synthetical hypogæic acid has the same properties as the natural acid in arachis oil found by *Gossmann and Scheven*, and by *Schroder*. *Meyer and Beer*, however, could not detect this acid. These observers state that the unsaturated fatty acids consist of oleic and linolic acids exclusively. *Hazura and Grüssner* further identified linolic acid. *Farnsteiner* calculated the amount of this acid in an arachis oil having the iodine value 82·9, as about 6 per cent of the mixed fatty acids. Judging from the iodine value of the liquid fatty acids, as given in the table of characteristics of the insoluble fatty acids, this proportion appears much too low. In somewhat better agreement with the numbers given in the table is *Farnsteiner's* statement, that the insoluble fatty acids contain, besides oleic acid, 30·3 per cent of liquid fatty acids, of which linolic acid only forms a fraction. Since arachis oil contains no linolenic acid, the deficiency of unsaturated acids (to account for the high iodine value of the insoluble liquid fatty acids) may perhaps be explained, pending further investigation, by the assumption that hypogæic tetrabromide is soluble in petroleum ether ; it may also be explained by *Rollet's* theory (cp. Vol. I. p. 198).

The true acetyl value of a sample of arachis oil of the acid value 2·17 was 9·02 to 9·09 (*Lewkowitsch*). The "cold-drawn" oils contain only small amounts of free fatty acids ; in commercial oils it is somewhat higher. In the following table I collate a number of observations :—

No	Description of Oil.	Number of Samples.	Free Fatty Acids, in terms of Oleic Acid	Observer.
			Per cent.	
1	Expressed, salad oil .	13	0·85 to 3·91	Nordlinger
2	Expressed, commercial oil	12	3·58 to 10·61	,,
3	Extracted oil . . .	16	0·95 to 8·85	,,
4	Refined oil . . .	1	0·62	Thomson and Ballantyne
5	Commercial oil . .	1	6·20	,,
6	Indian oil . . .	1	2·9	Crossley and Le Sueur
7	,, ,, . . .	1	4·8	,,
8	,, ,, . . .	1	16·5	,,
9	,, ,, . . .	1	13·1	,,

Oils No. 4 and No. 5 contained 0·54 and 0·94 per cent of unsaponifiable matter respectively. Oils No. 6, 7, 8, 9, showed in a Laurent polarimeter, in a 200 mm. tube the rotations –0°7′, +0°24′, ±0°0′, and –0°7′ respectively ; the optical activity cannot, therefore, be caused by the glycerides themselves.

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[1] *Liebig's Annal.*, 244, 253 ; *Berichte*, 1888, 878.
[2] *Monatsh. f. Chem.* 10, 242.

Physical and Chemical Characteristics of Arachis Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.	
At ° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·9171 [1] — Thomson and Ballantyne			189·3 [1]	Thomson and Ballantyne		
,,	0·9200 [2][3] — De Negri and Fabris			193·1 [2]	De Negri and Fabris	95-95·4 [2]	De Negri and Fabris
,,	0·9165 [4]			191·4-192 [3]	,,	97·9-100 [3]	,,
,,	0·917 [7] — Sadtler			189·4 [4]	,,	92·92·7 [4]	,,
,,	0·9175 [8] — ,,					90·2	Lewkowitsch
						101-105	Oliveri
15·5 (water 15·5=1)	0·9256 [6] — Crossley and Le Sueur			185·6-194·8 [6]	Crossley and Le Sueur	92·4	Crossley and Le Sueur
						100·82 [6]	Le Sueur
15·5	0·91795 — Lewkowitsch	0 to	Lewko-witsch	191-196	Oliveri	83·3-84·1 [5]	Tortelli and Ruggeri
20	0·9118-0·9125 [9] — Wijs	+2 [6]	Sadtler	194-196	Thorner	84·6 [6]	Sadtler
,,	0·9139-0·9145 [7] — ,,	+3 [7]	,,			91·75 [7]	,,
,,	0·9153 [10]	+3 [8]	,,			94·17 [8]	,,
99 (water 15·5=1)	0·8673 — Allen	+2 [9]					

[1] Refined oil.   [2] From Pondichéry nuts.   [3] From Coromandel nuts.

[4] From Mozambique nuts.   [5] From Rufisque nuts.

[6] East Indian oils; the acid value of these oils, four in number, are recorded in the table, p. 306.

[7] Virginian nuts, *Amer. Journ. Pharm.*, 1897, 69, 490.   [8] Spanish nuts. *Amer. Journ. Pharm.*, 1897, 69, 490.

[9] African nuts.   [10] Egyptian nuts.

Physical and Chemical Characteristics of Arachis Oil—continued

Maumené Test		Refractive Index			Oleo-refractometer		Butyro-refractometer			Viscosity	
°C.	Observer.	At ° C		Observer.	"Degrees" at 22° C.	Observer	At ° C	"Degrees."	Observer.	No. of Seconds At 70° F.	Observer.
56·75	Sadtler	15	1·4731	Procter	+3·5⁴ to +6·5⁵	Jean	15·5	70-71·3	Tolman and Munson	350·1⁶	Crossley and Le Sueur
49¹	De Negri and Fahris⁷	15.5	1·4723	Tolman and Munson	+4	Bruyn and van Leent	25	66·5	Beckurts and Seiler	347·0	,,
51²	,,	20	1·4698	Harvey	+5 to +7	Pearmain	40	57·5	Crossley and Le Sueur	429·3	,,
46³	,,	60	1·4545	Thörner						306·9	,,

¹ From Pondichéry nuts.   ² From Coromandel nuts.   ³ From Mozambique nuts.
⁴ From Rufisque nuts.   ⁵ From Bonlam nuts.
⁶ East Indian oils; the acid values of these oils, four in number, are recorded in the table p. 306
⁷ By Jean's thermelæometer.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.			Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	At ° C.	Ob-server.	° C.	Observer.		° C.	Observer.	Mgms KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
94·87⁹	Sadtler	99 (water 15·5=1)	Allen	29-29·5	Dietrich		31·5-32 31·32 to 34·35	Dietrich Bense-mann⁴ Bach	201·6	Thorner	281·8	Allen	95·5-96·9	Morawski and Demski	1·4461	Thörner
95·31⁸	,,	0·8790 (water 100=1)	Arch-butt				33	Schoen					103·4²	De Negri and Fabrs		
							30						96-97	Thorner		
		25-23·1	De Negri and Fabrs		29-31·1	De Negri and Fabrs						Iodine Value of the Liquid Fatty Acids.			
		25·22·2	,,		28-30·2	,,						128·5	Wallenstein and Finck		
		24-22·1	,,		27-29·1	,,						122·4-123·4·5	Tortelli and Ruggeri		
		29-30	Thorner		34·ᵡ	Sadtler						104·7-105·5⁶	,,		
		32·5·8	Sadtler		29·9	,,						106·7	,,		
		27·5·7	,,	Titer Test.											
		28·1-29·2	Lewko-witsch												

1 From Pondichery nuts.   2 From Coromandel nuts.   3 From Mozambique nuts.   4 Bensemann's method   5 Iodine value of oils: 92·2-93·5.
6 From Rufisque nuts; iodine value of oil: 83·3-84·1.   7 From Gambia nuts; iodine value of oil   84·6.   8 Spanish nuts.   9 Virginia nuts.

Arachis oil can be identified and detected with certainty by the isolation of " arachidic acid," which represents a mixture of arachidic and lignoceric acids, and will be termed here " crude arachidic acid."

The method originally proposed by *Renard* [1] is carried out in the following manner :—Saponify 10 grms. of the oil, separate the fatty acids from ,the soap solution by hydrochloric acid, dissolve them in 90 per cent alcohol, and add a solution of lead acetate. The author shortens the process by neutralising the excess of alkali with acetic acid, using phenolphthalein as an indicator, and precipitating with lead acetate without previously isolating the fatty acids.[2] Filter off the precipitated lead salts, and separate the lead salts of the unsaturated acids from those of the saturated fatty acids (as described Vol. I. p. 545). Decompose the latter with hydrochloric acid under ether, separate the ethereal layer of the fatty acids and distil off the ether. Next dissolve the residue in 50 c.c. of hot 90 per cent (by volume) alcohol. On cooling the alcoholic solution " crude arachidic acid " separates out in a crystalline form. Filter the crystals off and wash on the filter, first with a measured quantity of 90 per cent, then with 70 per cent (by volume) alcohol (which dissolves but small quantities), and finally pour boiling absolute alcohol on the filter, receiving the filtrate in a porcelain dish or in a flask. Evaporate to dryness and weigh the residue. Add to the weight of crude arachidic acid thus found the quantity dissolved by the 90 per cent alcohol, taking as basis for calculation that 100 c.c. dissolve 0·022 grm. at 15° C., or 0·045 grm. at 20° C. Finally determine the melting point of the crude arachidic acid ; it should be from 71° to 72° C. *Renard* isolated 4·5 to 5·0 per cent, *Allen* 5·5, and *De Negri and Fabris* 4·37 to 4·80 per cent of " arachidic acid " from samples of genuine arachis oil. Hence the amount of acid found represents approximately $\frac{1}{20}$ of the arachis oil. By multiplying the weight of the crude arachidic acid found in a sample by 20 the amount of arachis oil actually present is derived. *Bellier* [3] proposes the factor 23·81.

De Negri and Fabris [4] obtained the following numbers from mixtures of olive oil and arachis oil.

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[1] *Compt. rend.*, 1871 (73), 1330.
[2] Kreis (*Journ. Soc. Chem. Ind.*, 1895, 688) suggests the use of an *alcoholic* solution of lead acetate.
[3] *Ann. chim. anal. appl.*, 1899 [4], 4.
[4] *Annali del Laboratorio Chimico delle Gabelle*, 1891-92, 123.

Sample containing		Crude Arachidic Acid found.			Arachis Oil found.
Olive Oil.	Arachis Oil.	Weighed as Crystals.	Calculated as dissolved.	Total.	Per cent.
Per cent.	Per cent.	Grms.	Grms.	Grms.	
70	30	0·107	0·0315	0·1385	29·08
80	20	0·0605	0 0315	0·0920	20·24
85	15	0·0385	0 0315	0·070	14·00
90	10	0·0200	0·0315	0·0515	10·30
90	10	traces			
90	10	0·0280	0·0154	0·0434	9·54
90	10	traces			

It will thus be seen that by using 10 grms. of a suspected olive oil, the limit of accuracy is reached if it contain only 10 per cent of arachis oil. Therefore from 20 to 40 grms. of a sample should be employed ; the proportions of 90 per cent alcohol must then be doubled or quadrupled.

Tortelli and Ruggeri,[1] in an exhaustive examination of *Renard's* method, found that the solubilities in 90 per cent alcohol given by *Renard* are too low. Their method leads to a crude arachidic acid (see below) melting from 74-75·5° C. ; for this acid the following solubilities were ascertained :—

100 *c.c. of* 90 *per cent Alcohol dissolve Crude Acid of M.P.* 74°-75·5° *C.*

Amount of Acid taken.	Melting Point.	Amount of Acid dissolved			The amount of Crude Acid employed corresponds to
		At 15° C.	17·5° C.	20° C.	
Grms.	° C.	Grms.	Grms.	Grms.	
2·7000	74·3-74·5	0 0729	0 0820	0 0910	
1·5600	75·1-75 5	0·0715	0 0801	0 0922	More than 20 grms of arachis oil
1·2506	74·8-75·5	0·0730	0 0811	0·0902	
1·0000	74·3-74 5	0 0688	0 0866	0·0914	
0·9604	74·0-74 6	0·0680	0·0869	0·0918	About 20 grms of arachis oil
0·5503	74 0-74 6	0 0650	0·0806	0·0879	Mixtures containing about 50 per
0·5008	74 0-74 6	0·0643	0 0799	0·0844	cent of arachis oil
0 3899	74·4-75 5	0·0602	0·0673	0 0740	Mixtures containing 40 per cent of arachis oil
0·2615	74-75	0·0539	0·0610	0 0680	Mixtures containing 27 per cent of arachis oil
0·1690	74-75	0 0447	0·0544	0 0662	Mixtures containing 18 per cent of arachis oil
0·1064	74-75	0·0343	0·0402	0·0472	Mixtures containing 11 per cent of arachis oil
0·0504	74 7-75·5	0·0301	0·0398	...	Mixtures containing 5 per cent of arachis oil
0·0505	74 2-74·6	0·0314	0·0410	..	

For practical purposes these numbers may be summarised as follows :—

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[1] *Journ. Soc. Chem. Ind.*, 1898, 877.

100 c.c. of 90 *per cent Alcohol dissolve Crude Acid of M.P.* 74°-75·5° C.

For Amount of Acid.	At 15° C.	17·5° C.	20° C.
From 2·7 down to 0·5 grms.	0·070	0·080	0·090
„ 0·47 „ 0·17 „	0·050	0·060	0·070
„ 0·11 „ 0·05 „	0·033	0·040	0·045

In order to obtain crude arachidic acid of the melting point 74°-75·5° C. *Tortelli and Ruggeri* modify the *Renard* test as follows :—The lead salts of the solid fatty acids are prepared from 20 grms. of oil as described above, the liberated solid acids dissolved in 100 c.c. of 90 per cent alcohol by warming on the water-bath to about 60° C. (if a slight turbidity is noticed one drop of very dilute hydrochloric acid is added) and allowed to stand for three hours at 15° to 20° C. The separated acid is thrown on a filter, the filtered alcoholic solution being used to transfer the crystals completely on to the filter. The crystals are washed three times each with 10 c.c. of 90 per cent alcohol, and then several times with 70 per cent alcohol. The crystals on the filter are dissolved in boiling absolute alcohol, the solution is received in a flask, the alcohol distilled off, the residue dissolved in 100 c.c. of 90 per cent alcohol as described already, and the crystals washed on a filter with 90 per cent and 70 per cent alcohol, exactly as before. The washing with 70 per cent alcohol is finished when the wash-alcohol no longer dissolves appreciable quantities.[1] Finally the crystals are dissolved in absolute alcohol, and their weight is determined.

The crystals should melt between 74° and 75·5° C. On observing the alcoholic solution of the solid fatty acids when taken from the water-bath to cool, it will be readily noticed that the crystals represent a mixture of arachidic and lignoceric acids. At first very fine, lustrous needles separate in tufts—lignoceric acid ; afterwards there appear larger quantities of very thin, shining laminæ of nacreous lustre— arachidic acid. The separation commences in the case of pure arachis oil at about 35° to 38° C., the temperature of crystallisation falling as the proportion of arachis oil in a given sample decreases (cp. table p. 313). The following table gives the amounts of " arachidic acid " found in some arachis oils by *Tortelli and Ruggeri* :—

---

[1] E. Bertainchand recommends to carry out the washing operations with the aid of a vacuum. *Annal. des falsif.*, 1910, 57.

Crude Arachidic Acid found in Arachis Oils

Source of Oil	Crude Acid	
	Per cent.	Melting Point. °C
Buenos Ayres, expressed at 45° to 50° C.	5·24	74 4-74·7
,, extracted with ether	4·92	74 2-74·8
Rufisque, first expression	4·31	74·2-74 6
,, second expression	4·55	74·4-75 2
Gambia, first expression	4·59	74·5-75 1
Commercial, French	5·33	74·1-74·4
,, Spanish	5·40	74·3-75·4

For practical purposes 4·8 per cent may be taken as the mean proportion of crude arachidic acid, melting point 74°-75·5° C. in commercial arachis oils.

The following table, due to *Tortelli and Ruggeri*, may serve as a corollary to the numbers given by *De Negri and Fabris* (see above p. 311).

Sample containing		Temperature at which crystals separate from 90 per cent Alcohol.		Crude Arachidic Acid.				M P of Crystals	Arachis Oil found (approx)
Olive Oil	Arachis Oil	°C	90 per cent Alcohol used	Weighed as Crystals.	Dissolved (calculated)	Total.			
Per cent.	Per cent.	°C	c.c.	Grms	Grms.	Grms.	Per cent.	°C.	Per cent.
0	100	37 7	260 at 15° C	0·8894	0 1768	1 0662	5 33	74·1-74 3	100
40	60	31 8	150 ,, 17 5	0 5231	0 1200	0 6431	3 22	74-74 6	60
50	50	29 0	250 ,, 75	0 3931	0 1500	0 5431	2 72	74-74 6	50
60	40	25 5	280 ,, 75	0 2770	0 1509	0 4279	2·14	74 5-75 1	40
70	30	23 2	260 ,, 75	0 2056	0 1300	0 3356	1 68	74 1-74 6	31
80	20	21 0	200 ,, 75	0 1200	0 1150	0 2110	1 21	73 9-74 4	22
90	10	18 8	220 ,, 15	0 0514	0 0682	0 1196	0 60	72 2-74 6	11
95	5	16 7	150 ,, 15	0 0241	0 0434	0 0675	0 34	73-73·5	6·7

Archbutt,[1] confirming *Tortelli and Ruggeri's* figures, computes the following corrections :—

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[1] *Journ. Soc. Chem. Ind.*, 1898, 1124.

[TABLE

Correction per 100 *c.c. of* 90 *per cent Alcohol used for Crystallisation and Washing*

For Weights of Fatty Acids obtained by Renard's Process	Grms at		
	15° C.	17·5° C.	20° C.
0·1 or less . .	+0·033	+0·039	+0·046
0·2 ,, . .	0 048	0·056	0 064
0 3 ,, . .	0 055	0·064	0·074
0·4 ,, . .	0·061	0·070	0·080
0·5 ,, . .	0·064	0 075	0·085
0·6 ,, . .	0·067	0·077	0·088
0·7 ,, . .	0·069	0·079	0·090
0·8 ,, . .	0·070	0·080	0·091
0·9 and upwards .	0 071	0 081	0 091

Archbutt recommends the following modification of *Renard's* process :—Dissolve the fatty acids obtained from 10 grms. of oil [by decomposing the saponified mass with hydrochloric acid under ether and evaporating off the solvent] in 50 c.c. of 90 per cent alcohol ; add to the solution, which must not be allowed to cool below 38° (to prevent separation of crystals) 5 c.c. of a 20 per cent aqueous solution of lead acetate, cool to about 15° C., agitate, allow to stand for half an hour, filter and wash once with ether. Return the soaps into the flask with the aid of ether, digest with ether and repeat this operation three times ; lead oleate is thus dissolved out entirely. Transfer the solid soap with the aid of ether into a separating funnel, decompose with hydrochloric acid and wash the ethereal layer until free from mineral acid Distil off the ether, dry the fatty acids in a water oven, and pour into the flask 50 c.c. of alcohol of exactly 90 per cent (spec. grav. 0·8340). Dissolve the fatty acids by warming the (corked) flask, allow to cool to either 15° C. or 20° C., collect the crystals on a small filter (or preferably on a *Gooch* crucible), and wash three times with 10 c.c. of 90 per cent alcohol, each time at the same fixed temperature. The filtrate and washings are measured ; the necessary corrections are found in the table given above.

The crystals are thoroughly washed with 70 per cent alcohol, in which the crude arachidic acid is quite insoluble, until the washings remain clear on adding water. It is not necessary, although advisable, to redissolve the acids in 50 c.c. of 90 per cent alcohol and repeat the operations just described. The crystals are dissolved in boiling ether and weighed after drying at 100° C. The correction is then added to the weight. The melting point (capillary tube method) of the mixed arachidic and lignoceric acids so isolated varied from 71° to 72·5° C., but even when working in exact accordance with *Tortelli and Ruggeri's* directions crystals melting at 74°-75° C. could not be obtained by *Archbutt*, his highest figure being 73·3° C. [It may be added that after recrystallising the acids repeatedly from 90 per cent alcohol the melting point was raised to 79·6° C.]

The following table shows in greater completeness the results obtained by *Archbutt* with one and the same sample of arachis oil :—

Estimation of Arachidic and Lignoceric Acids by different Methods in one and the same Sample of Arachis Oil

Weight of Oil taken	Method.	Volume of Alcohol. Temperature, °C / Solubility Coefficient	Crude Arachidic Acid. Dissolved in the Alcohol.	Weighed.	Total.	Per cent.	Melting Point by Capillary Tube Method.
Grms. 10	Renard's; 2 grms. PbĀ₂ aq.; not re-crystallised.	70 c.c. 20° 0·082	0·0574	0·4283	0·4857	4·86	°C. 71
10	Renard's; 4 grms. PbĀ₂ aq.; not re-crystallised.	70 c.c. 20° 0·082	0·0574	0·4258	0·4832	4·83	71
10	Renard's; 1 grm. PbĀ₂ aq.; not re-crystallised.	80 c.c. 15° 0·0625	0·0500	0·4480	0·4980	4·98	71
10	Renard's; 2 grms. PbĀ₂ aq., not re crystallised.	90 c.c. 15° 0·063	0·0567	0·4554	0·5121	5·12	70
10	Renard's; 1 grm. PbĀ₂ aq.; recrystallised	130 c.c. 15° 0·061	0·0793	0·3931	0·4724	4·72	71
10	Renard's; 1 grm. PbĀ₂ aq.; recrystallised.	135 c.c. 15° 0·061	0·0823	0·4125	0·4948	4·95	72
20	Tortelli's; exactly as described in *Chem. Zeit*, 1898, 600.	265 c.c. 17·5° 0·079	0·2094	0·6935	0·9029	4·51	72
20	Renard's; 2 grms PbĀ₂ aq.; recrystallised; Gooch filter used	250 c.c. 15° 0·070	0·1750	0·7649	0·9399	4·70	72·5
20	Renard's; 2 grms. PbĀ₂ aq.; recrystallised; Gooch filter used	240 c.c. 15° 0·070	0·1680	0·7718	0·9398	4·70	72 72·8-72·3 (Bensemann)
20	Tortelli's; exactly as described; Gooch filter used	248 c.c. 15° 0·069	0·1711	0·6967	0·8678	4·34	72 72·3-73·3 (Bensemann)

The accuracy attainable in practical cases is shown by the following table :—

Results of Analysis of Mixtures of Olive Oil and Arachis Oil

Composition of Oil taken.		Volume of 90 per cent Alcohol.	Crude Arachidic Acid.					Arachis Oil found.
Olive Oil.	Arachis Oil.	Temperature. Solubility Coefficient.	Dissolved in the Alcohol.	Weighed.	Total.	Per cent.	Melting Point.	
Per cent.	Per cent.						°C.	Per cent.
...	100	80 c.c. 15° 0 0625	0·0500	0·4480	0·4980	4·98	71	...
90	10	73 c.c. 15° 0 033	0·0241	0·0265	0·0506	0·506	71	10·2
80	20	73 c.c. 15° 0 033	0·0241	0 0715	0·0956	0·956	71	19·2

Tortelli and Ruggeri [1] maintain, however, that their modification is less cumbersome and leads to more correct results than the one suggested by *Archbutt*.

The importance of the detection of arachis oil in olive oil has led to a renewed study of the quantitative methods (in *Archbutt's* laboratory) by *N. Evers*,[2] who recommends the following working process, the details of which must be observed most minutely in order to obtain reliable results :—5 grms. of the sample of oil are saponified by boiling for about five minutes under a reflux condenser with 25 c.c. of alcoholic potash (80 grms. of potassium hydrate, pure from alcohol, dissolved in 80 c.c. of water, and made up to 1000 c.c. with 90 per cent [by volume] alcohol). To the hot soap solution are added 7·5 c.c. of acetic acid prepared by mixing one volume of glacial acetic acid with two volumes of water, and 100 c.c. of 70 per cent (by volume) alcohol containing one per cent (by volume) of hydrochloric acid. The solution is cooled to 12°-14° C. for one hour. The separated crystals are filtered and washed with 70 per cent (by volume) alcohol containing one per cent of hydrochloric acid at 17°-19° C., the precipitate is broken up occasionally by means of a looped platinum wire, and washed until the filtrate gives no turbidity with water. The wash-waters are measured. The precipitate is dissolved, according to its bulk, in 25 to 70 c.c. of hot 90 per cent (by volume) alcohol, and cooled to a fixed temperature between 15° and 20° C. The solution is allowed to stand at the fixed temperature for from one to three hours. The crystals are filtered off, washed with a measured volume of 90 per cent (by volume) alcohol (about half the volume used for crystallisation) and finally with 50 c.c.

[1] *Moniteur Scientif.*, 1902 [4], 215 ; cp. also Perrin, *Moniteur Scientif.*, 1901 [4], 320.
[2] *Analyst*, 1912, 487.

of 70 per cent alcohol.   They are rinsed with warm ether into a
weighed flask, the ether is distilled off, and the residue dried at 100° C.
and weighed.   If the melting point is lower than 71° C., the acid is re-
crystallised from 90 per cent (by volume) alcohol.   The correction for
the solubility in 90 per cent alcohol is added exactly as in *Renard's*
process, as also the correction for the total volume of 70 per cent
alcohol used in precipitating and washing.

The correction required for the 70 per cent alcohol (which is ignored
in *Renard's* original process) is taken from the following table due to
Evers :—

Weight of Acids (corrected for 90 per cent Alcohol)	Correction per 100 c.c., 70 per cent Alcohol.		
	Melting Point 71° C.	Melting Point 72° C.	Melting Point 73° C.
	Grms.	Grms.	Grms.
Above 0·10 grms.	0 013	0·008	0 006
0·08-0 10 ,,	0 011	0·007	0 006
0·05-0 08 ,,	0 009	0·007	0 005
0 02-0 05 ,,	0 007	0·006	0·005
Less than 0 02 ,,	0·006	0·005	0 004
Factor for conversion of percentage of fatty acids to arachis oil .	17	20	22

In the case of those oil mixtures containing arachis oil, which
yield no crystals from 90 per cent or a very small amount only, a suffi-
cient quantity of water is added to reduce the strength of alcohol to
70 per cent (31 c.c. of water per 100 c.c. of 90 per cent alcohol).   The
crystallisation is allowed to take place at 17°-19° C. for one hour ; the
crystals are washed, and the correction for 70 per cent alcohol is added.
Should the melting point of crude arachidic acid be below 71° C., then
it is recrystallised from a small quantity of 90 per cent alcohol, or from
70 per cent alcohol.   In the following table due to *Evers*, the results
obtainable by this method are set out .—

[Table

Oil.	Alcohol used for crystallisation.	Weight of Crystals.	Correction for 90 per cent Alcohol.	Correction for 70 per cent Alcohol.	Total.	Per cent.	Melting Point °C.	Per cent of Arachis Oil by Factor.
	Percent							
Arachis (A)	90	0 160	0·040	0·027	0·227	4·54	73	100
	70	0·218	..	0·065	0·283	5 66	71	96
Arachis (B)	90	0·163	0 045	0·032	0·240	4 80	72	96
	70	0·233	..	0·068	0·301	6·02	71	102
Arachis (C)	90	0·152	0·054	0 034	0·240	4·80	72	96
Arachis (D)	90	0·194	0 033	0·028	0·255	5·10	72	102
Arachis (A), 50% Olive "Nice," 50%	90	0·056	0 032	0 022	0·110	2·20	73	48
	70	0·090	..	0·055	0·145	2·90	71	49
Arachis (A), 35% Olive "Nice," 65%	90	0·045	0 020	0·029	0 094	1·88	71	32
	90	0·029	0 040	0·020	0·089	1·78	72·5	37
	70	0·059	..	0·040	0·099	1·98	71	34
Arachis (A), 20% Olive "Nice," 80%	90	0·024	0·012	0·019	0·055	1·10	71	19
	70	0·030	..	0·024	0·054	1·08	71	18
Arachis (C), 20% Olive "Malaga," 80%	90	0·012	0·020	0·015	0·047	0·94	72	19
	70	0·021	..	0 027	0·048	0·96	71	16
Arachis (A), 10% Olive "Nice," 90%	90	0·009 [1]	0·008	0 008	0·025	0·50	73	11
	70	0·008	..	0·015 [2]	0·023	0·46	70	8
Arachis (B), 10% Olive "Nice," 90%	90	0	..	..	..	0	..	..
	70	0·012	..	0·018	0 030	0·60	71	10
Arachis (C), 10% Olivo "Malaga," 90%	90	0	..	..	..	0	..	..
	70	0·011	..	0·016	0·027	0 54	71	9
Arachis (A), 5% Olivo "Nice," 95%	70	0·007	..	0·012	0·019	0·38	..	6·5
Sesamé	90	0	..	..	..	0	..	..
	70	0·012	..	..	..	0·24	64	..
Cotton seed	90	0	..	..	..	0	..	..
	70	0 006	..	..	..	0·12	50·55	..
Olive "saponified"	90	0·014	..	..	..	0·28	64·67	..
	70	0·021	..	..	..	0 42	64·68	..

For *Tolman's* modification of *Renard's* test as applied to solid fats containing cotton seed oil the reader must be referred to the original paper.[3]

The determination of the crude arachidic acid is of the greatest importance in the examination of olive oils suspected of being adulterated with arachis oil, for the latter so closely resembles olive oil in its characteristics that judiciously prepared mixtures cannot be detected with certainty by means of the usual quantitative reactions. For although, as a rule, arachis oil has a higher iodine value than olive oil, there are, in commerce, arachis oils the iodine values of which approach closely those of olive oils having exceptionally high iodine values. The quantity of arachidic acid naturally occurring in olive oil is too small to invalidate the correctness of *Renard's* method. Nor would an admixture of rape oil seriously interfere with the information

[1] This result was obtained by recrystallising the fatty acids obtained from 70 per cent alcohol, from 10 c.c. of 90 per cent alcohol.

[2] In these cases the correction has been added for melting point 71° C.

[3] Cp. W. B. Smith, *Journ. Amer. Chem. Soc.*, 1907 [29], 1756.

furnished by *Renard's* test, as special experiments, made in the author's laboratory, have shown. These experiments have been confirmed by *Archbutt's* determination of arachidic acid in rape oil (see also below p. 363, under " Olive Oil ").

Since the adulteration of olive oil with arachis oil has become of frequent occurrence (especially in those years when olive oil was high in price), the somewhat lengthy quantitative determination of arachidic acid has led to proposals to detect it qualitatively. Such tests (which are in truth nothing else than abbreviations of the quantitative method detailed above) were suggested by *J. Bellier*,[1] and modified by *Mansfeld*,[2] *Alder*,[3] and *Franz*.[4]

N. Evers[5] has tested these modifications and found them satisfactory. The qualitative test is carried out as follows :—1 c.c. of oil measured off accurately is saponified with 5 c.c. of alcoholic potash prepared from 80 grms. of potassium hydrate, pure from alcohol, dissolved in 80 c.c. of water and made up to 1000 c.c. with a 90 per cent (by volume) alcoholic solution, and saponified over a boiling water bath for exactly four minutes in a 100 c.c. flask fitted with a condensing tube. Loss of alcohol by evaporation is thereby avoided. The solution is cooled down to about 15° C. and exactly 1·5 c.c. of a dilute acetic acid (prepared from one volume of glacial acetic acid and two volumes of water) as also 50 c.c of a 70 per cent (by volume) alcohol are added and shaken until the solution has become clear. In case the solution is turbid (which is due to a somewhat high proportion of arachis oil), the liquid is warmed until the turbidity has disappeared. The solution is then immersed in cold water, whilst being shaken, until the temperature is exactly 16° C. It is shaken at 16° C for five minutes, and in case no distinct turbidity should have appeared, the temperature is lowered to 15·5° C. ; the same operation is repeated and again five minutes allowed to elapse.

Evers confirms *Bellier's* statement that a distinct turbidity is produced by 5 per cent of arachis oil in the sample. The author would deprecate this qualitative test, as in the present state of our knowledge tests of this kind cannot be pronounced to be reliable. Thus *Archbutt*[6] found that certain neutralised " residuum olive oils " gave a precipitate, perhaps owing to a certain amount of unsaponifiable matter, of which these particular oils contain a considerable amount, separating out. At any rate, far too few observations have been made to justify the non-application of qualitative tests.

By catalytic reduction arachis oil is converted into a hard fat, the iodine value and consistence of which depend on the length of time employed in the reduction. By the catalytic reduction of the mixed

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[1] *Ann. Chim. anal.*, 1899 (4), 4 ; cp. also Guarnieri, *Staz. sperim agrar. ital.* (42), 108.

[2] *Zeits. f. Unters. d Nahrgs- u. Genussm.*, 1905 (17), 57.

[3] *Ibid.*, 1912 (24), 676 ; cp. also H. Luers, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1912 (24), 683.

[4] *Beitrage z. Nachweis u. z. Kenntniss d. Erdnussöles*, Dissert., Munchen, 1910.

[5] *Analyst*, 1912, 487.

[6] *Journ. Soc. Chem. Ind.*, 1911, 5.

fatty acids, oleic and linolic acids are reduced to stearic acids, and hypogæic acid to palmitic acid. Thus an indirect method of examining arachis oil would be given by reducing catalytically the mixed fatty acids when stearic and arachidic acids can be separated off completely, whilst palmitic acid would remain in the stearic acid solution.

If this appears too complicated, the solid acids may be separated from the liquid acids by the lead-salt-ether method, when the liquid fatty acids can be reduced catalytically to stearic and palmitic acids, which may then be separated by the method given under stearic acid in Vol. I. p. 557.

H. Kreis and E. Roth[1] have especially shown (although it was obvious) that the arachidic acid can be determined in "hardened" arachis oil in the same manner as is done in ordinary arachis oil.

Bömer[2] fractionated a hydrogenised (hardened) arachis oil by crystallisation from ether, and obtained after nineteen recrystallisations 2-3 per cent of a glyceride melting at 68·1° C. The fatty acid obtained from the nineteenth fraction melted at 68·6° C. *Bömer* suggests that the glyceride so obtained represents tristearin. In view of the remarks made by the author Vol. I. p. 559, the absence of arachidic acid must be proved before this conclusion can be accepted.

Arachis oil is not infrequently adulterated with poppy seed, sesamé, cotton seed, and rape oils.

Poppy seed oil is indicated by a high iodine value and high specific gravity of the sample.

Sesamé oil is recognised by the furfural reaction. It has been pointed out above (p. 221) that a faint *Baudouin* colour reaction does not necessarily indicate adulteration. As arachis oil is mostly pressed in the same works where sesamé oil is expressed, slight colouration may be expected.[3] In doubtful cases it is advisable to determine the iodine value of the oil, as also of its liquid fatty acids, the solidifying point of the insoluble fatty acids, and in important cases the proportion of arachidic acid.

Cotton seed oil is detected by the same quantitative reactions; the colour reactions described above (p. 203) serve as confirmatory tests.

Rape oil is revealed by a lower saponification value of the oil than the normal one, by low solidifying and melting points of the mixed fatty acids, and by the isolation of behenic acid (cp. Vol. I. p. 553).

Nitrobenzene, used as an adulterant in Porto Rico, is determined by shaking the oil with zinc dust and hydrochloric acid, and removing the aniline formed by washing out with water.[4]

Very large quantities of arachis oil are expressed in the South of France; considerable quantities are also prepared in Valencia (Spain), in Trieste, and in Holland. In this country as yet no arachis oil is made. It has been pointed out already that the oils of first expression are used as salad oils. They are largely employed for adulterating, or

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1913, 81.

[2] *Chem. Revue*, 1912, 247.

[3] Cp L. Derlin, *Chem. Zentralbl.*, 1910 (I.), 1812.

[4] Lucas, *Journ. Ind. and Eng. Chem.*, 1913, 576.

even wholly substituting, olive oils, also for blending with olive oil; thus the Valencia oil is specially known to be mixed with Andalusian olive oil, in order to neutralise the harsh flavour of the latter. Edible arachis oil is also used for preserving sardines. The oils of the second and third expressions are chiefly used in soapmaking in the South of Europe. One of the characteristic components of the Marseilles white soap is arachis oil; it is not used in the manufacture of the mottled ("marbled") Marseilles soap.

RICE OIL [1]

French—*Huile de riz.*   German—*Reisol.*   Italian—*Olio di riso.*

For tables of characteristics see p. 322.

This oil, as obtained in this country from Rangoon rice meal (from *Oryza sativa*, L.) by hydraulic pressure,[2] has a dirty greenish colour. Rangoon rice meal contains about 15 per cent of oil, common rice meal only 8-9 per cent.

Oil from fresh rice bran is practically neutral; on standing, the proportion of free fatty acids very rapidly increases owing to the action of an enzyme (*Browne* [3]).

The occurrence of an enzyme in rice bran was demonstrated by *Browne*, by mixing 20 c.c. of a 20 per cent cold aqueous extract of rice bran with an equal volume of castor oil. After twenty-four hours the emulsion became acid, and after one week the proportion of free fatty acids had risen to 16 per cent. It appears to the author likely that the action of the lipase had been arrested in this experiment, as *Browne* had rendered the mixture faintly alkaline to litmus. Further proof of the view that the production of free fatty acids is due to an enzyme is given by an experiment, in which freshly ground rice bran was divided into two portions, one of which was heated to 100° C. to destroy the enzyme.[4]   After one month the oil was extracted from both samples. The results of this experiment are reproduced in the following table:—

	Free Acid as Oleic Acid. Per cent.
Raw rice (stored many months) . . .	6·9
Fresh bran (six hours after grinding) . . .	12·5
Bran, one month old, unheated . . .	62·2
„ „ heated . . .	24·0

According to *Tsujimoto* [5] the fatty acids consist of:—palmitic acid 20 per cent, oleic acid 45 per cent, linolic acid 35 per cent.

An attempt to put the oil obtained from rice bran to commercial use was made some years ago in Louisiana.[6]   The industry disappeared,

[1] Smetham, *Journ. Soc. Chem. Ind.*, 1893, 848.
[2] Cp. French patent 415,226 (Société Hercules et Cie).
[3] *Journ. Soc. Chem. Ind.*, 1903, 1137.
[4] Cp. also J. Shimanzono, *Arch. experiment. Pathol. u. Pharmakol.*, 1911 (65), 361.
[5] *Chem. Revue*, 1911, 112.
[6] Cp. "Rice Oil Industry, Louisiana," *Zeitschr. f. angew. Chem.*, 1905, 1239.

however, after a short time, no doubt owing to the comparatively low prices for oils and fats which ruled immediately after the venture had been set on foot. The recent rise in prices revived the commercial attempts to extract the oil in Italy and, in this country, Hull. An outlet for the oil is being sought in the soap industry.

Physical and Chemical Characteristics of Rice Oil

Specific Gravity.		Solidifying Point. °C.	Saponi- fication Value. Mgrms. KOH.	Iodine Value Per cent	Maumené Test °C.	Refractive Index. Butyro- refractometer. "Degrees." At 25° C.	Observer.
At °C.							
99 (water 99 = 1)	0·8907		193·2 193·5	96·4 91·65			Smetham Browne
15	0·923	2·1		106 5	66 7	68·2	Fabris [1] and Settimj
				107			Tsujimoto

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponi- fiable. Per cent.	Solidify- ing Point. °C.	Melting Point. °C.	Mean Molecular Weight	Observer	Iodine Value.	
					Per cent	Observer.
95·6	28-29	36 31-32	289 3	Browne F. and S.	97·4 109	Twitchell[2] F. and S.[3]

ARGAN OIL, MOROCCAN OLIVE OIL

French—*Huile d'Argan.* German—*Arganöl, Marokkanisches Olivenöl.*

Argan oil [4] is prepared in considerable quantities in Morocco from the fruits of *Arganum sideroxylon*, a tree growing in the south-west of Morocco. The fruit is the size of a small walnut, and yields an oil of a golden yellow colour, which simulates in odour and taste arachis oil. The oil serves the natives as an edible oil in preference to the home-grown olive oil; it is also used as a burning oil. The export of this oil had, up till recently, been forbidden by the sultans of Morocco. Specimens previously obtained in Europe were sold as Morocco olive oil, and were considered to represent true olive oil.

[1] The oil was extracted from Italian rice germs, and gave 30 per cent of solid and 70 per cent of liquid fatty acids.
[2] Private communication.   [3] Iodine value of liquid fatty acids 130·7.
[4] *Les Végétaux utiles de l'Afrique Tropicale Française*, par Aug. Chevalier.

The following characteristics havo been dotermined by *E. A. Sasserath* : [1]—

Specific gravity at 15° C. .	0·988
Saponification value	192·12
Iodine valuo	95·94
Insoluble fatty acids +unsaponifiablo	95·6 per cent

On shaking the oil with nitric acid, of the spec. grav. 1·4, a dark crimson colour is developed, which persists for about one hour. This characteristic colour reaction is stated to allow the differentiation of argan oil from olive oil (in addition to the information furnished by the iodine value).

TEA SEED OIL

French—*Huile de thé* ; *huile de camellia*.   German—*Theesamenol*.
Italian—*Olio di thè*.

For tables of characteristics see p. 325.

Tea seed oil is expressed on a large scale in China from the seeds of *Thea sasanqua*,[2] Nois (Thunb.), which is specially cultivated in China, Tonkin, and Assam for its fruits and not for its leaves. The first pressed oil serves thero as an edible oil,[3] although the proportion of saponin it contains would render it somewhat unsafe for consumption. The oil obtained by extraction with solvents is perfectly free from saponin ; [4] the lower qualities are used as burning oil and for soap-making. In commerce two varieties, viz. Chinese and Assam oil, aro obtainable. Chinese tea seed ·yields 30-35 per cent, Assam tea seed 43-45 per ccut, of a straw or ambcr coloured oil closely resembling olive oil. Like the latter it gives a hard elaïdin. The proportion of liquid fatty acids (by the lcad-salt-ether method) varies from 88 to 93·2 per cent (*Lane*).

The fatty oil from *Camellia oleifera*, Bot. Reg., a plant largely cultivated in China for the sake of the pale bland oil prepared from its seeds—" Cha-yow oil "—is not used for cdible purposes, but as a hair oil or a burning oil. Its specifio gravity is 0·9175 at 15° C.

The foregoing *résumé* of the notes published in the literature on tca seed oil must be accepted with reserve, as the statements regarding the origin of the oils examined by the various observers are extremcly indefinite. To a great extent they may be considered as superseded by the description of the following two oils: " Tsubaki Oil " and " Sasanqua Oil," which, notwithstanding their much lower iodine

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[1] *Zeits. f. Unters. d. Nahrgs· u. Genussm.*, 1910, xv. 749.

[2] Synonyms are : *Camellia drupifera*, Lour. ; *Thea oleosa*, Lour. ; *Thea drupifera*, Pierre ; *Camellia oleifera*, Wall. A specimen of oil from *Camellia drupifera*, Lour., originating from Cochin China, is stated by Pottier (*Les Nouveaux Remèdes*, 1900, 16, 121) to have the specific gravity 0·980 (!), and to rotate the plane of polarised light 1·8° to the right in a 200 mm. tube.

[3] The Jesuit D'Incarville about 1735 mentions already the use of this oil for edible purposes in China.

[4] Weil, *Arch. d. Pharm.* 239, 365.

values, are described here on account of their near relationship to the commercial tea seed oils mentioned above.

The seeds of the ordinary tea plant—*Thea sinensis*, Sims. = *Camellia theifera*—contain a fatty oil, but since in the cultivation for its tea leaves the development of the seed is mostly suppressed, the oil has no commercial importance. The seeds are round, and have a diameter of about 1 cm. Kernels obtained from Tokyo and Uji plants respectively, gave the following results :—Moisture, 15·60 per cent ; 6·46 per cent. Oil, 23·9 per cent ; 26·23 per cent. Ash, 2·6 per cent ; 2·5 per cent. The expressed oil from the Tokyo seed was an orange yellow liquid of somewhat unpleasant odour and bitter taste (acid value 0·74).

The following characteristics are given by *Tsujimoto* for Japanese oil : [1]—

Oil—

Specific gravity at 15° C.	0·9178
Solidifying point	– 10° C.
Saponification value	191·9
Iodine value	90·42
Reichert-Meissl value	0·66
Refractive index at 20° C.	1·4707

Fatty Acids—

Insoluble acids + unsaponifiable	95·6 per cent
Specific gravity at 98° C.	0·8445
Melting point	33·5° C.
Neutralisation value	197·6
Mean molecular weight	283·9
Iodine value	92·86

Seeds from Upper Assam yielded on extraction with petroleum ether 16·1 per cent of an oil having the following characteristics (*Menon* [2]) :—

Oil—

Specific gravity, 15/15° C.	0·9028
Saponification value	189·9
Reichert-Meissl value	0·56
Titration number of insoluble volatile acids	0·56 c.c.
Iodine value	92·7

Fatty Acids—

Insoluble fatty acids + unsaponifiable	2·6 per cent
Insoluble fatty acids	93·04 per cent
Melting point	38·9° C.
Neutralisation value	199·9
Mean molecular weight	280·5
Iodine value	94·13

The fatty acids consisted of about 25 per cent of solid acids melting at 57·8° C. and having the neutralisation value 209·8, mean molecular weight 2673, iodine value 13·84, and 74·75 per cent of liquid acids of the neutralisation value 191·1, mean molecular weight 293·5, and iodine value 117·8.

[1] *Chem. Revue*, 1908, 224.
[2] *Year-Book of Indian Guild of Science and Technol.*, 1912, 144.

Physical and Chemical Characteristics of Tea Seed Oil

	Specific Gravity			Solidifying Point		Saponification Value.		Iodine Value.		Refractive Index. Oleo-refractometer.	
	At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	"Degrees."	Observer.
Chinese oil	15	0·917-0·927	Schaedler	-5	Schaedler	195·5	Davies	88	Italie	+8 at 22° C.	Pearmain
Assam oil	15	0·920	Italie [1]	-12	Italie	194	Italie	90·49	Lane		
Japanese oil	20	0·9110	Wijs [2]			188·3	Wijs	88·9	Wijs		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	Mgrms. KOH	Observer.		Observer.	Per cent.	Observer.
91·5	Italie	10·11	Wijs	195	Wijs	287·6	Wijs	90·8	Wijs
							Liquid Fatty Acids	99·6-104·4 [3]	Lane

[1] *Journ. Soc. Chem. Ind.*, 1894, 79.   [2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1903, 492.   [3] Calculated.

TSUBAKI OIL [1]

French—*Huile de tsubaki.*   German—*Tsubakiöl.*
Italian—*Olio di tsubaki.*

This oil is obtained from the seeds of *Theà japonica*, Nois (*Camellia japonica*, L.), the tsubaki tree grown in Japan for ornamental purposes on account of its beautiful flowers.   In certain parts of Japan it grows wild in such abundance that the seeds are worked up for the preparation of oil, as in the islands of Idzu, in the Shidzuoka prefecture and several prefectures of Kiushiu (Kumamoto, Nagasaki, Oita).   The fruit ripens in autumn, and the seeds fall to the ground.   The seed is 2·25 cm. long ; its weight varies from 1·2 to 3 grms.   A specimen from Oshima examined by *Tsujimoto* consisted of 41·5 per cent of husks and 58·5 per cent of kernels.   Kernels from different localities gave the following results :— Moisture, 4·24-4·93 per cent ; oil, 64·3-66·4 per cent ; ash, 1·6-1·75 per cent.

The seeds are dried by exposure to sunlight, crushed, steamed, and pressed twice in the wooden wedge press (" tatsugi ") usually employed in Japan.   Other manufacturers decorticate the seeds previous to pressing.   The whole seeds when pressed yield 15 per cent of oil (by volume).

The oil prepared from fresh seeds by pressing is pale yellow and practically odourless ; its taste is mild and pleasant.

Commercial tsubaki oil has a yellow colour, and a slight peculiar odour ;   the inferior, decidedly rancid grades vary from yellow to reddish yellow.   The following characteristics are given by *Tsujimoto* :—

	Cold-drawn Oil.	Commercial Oil.	Oil from Decorticated Seed.
Oil—			
Specific gravity at 15·5° C.	0·9159-0·9163	0·9161-0·9166.	0·9160
Saponification value .	190·6-192·6	180·9-190·6	191·9
Iodine value .	80·3-81·3	80·1-80·6	80·4
Reichert-Meissl .	0·5		
Refractive index at 20°	1·4682-1·4691	1·4691-1·4679	1·4687
Fatty Acids—			
Insoluble acids + unsaponifiable .	95·5%		
Specific gravity at 100° C. (water at 15°=1)	0·8402		
Melting point .	22° C.		
Neutralisation value .	197		
Mean molecular weight .	284		
Iodine value .	93·7		

The oil solidifies completely at – 15° C.   In Valenta's test it becomes turbid at 81° C.   In the elaïdin test it solidifies in two hours and yields after twenty-four hours a very hard mass.

[1] Tsujimoto, *Journ. Coll. Engin. Imp. Univ. Tokyo, Japan*, 1908, vol. iv. p. 75.

'The acid values of a number of cold drawn oils varied from 1·63 to 2·67 ; commercial samples have higher acid values, up to 8·8.

The mixed fatty acids yielded (by the lead-salt-ether method) 93·1 per cent of liquid acids of the iodine value 89. They seem to consist of oleic acid only, as they neither gave ether-insoluble compounds on bromination, nor sativic acid on oxidation (*Kametaka*).

Tsubaki oil being the highest priced of all Japanese vegetable oils, is largely adulterated with rape, cotton seed, soya bean, and arachis oils. *Tsujimoto* finds *Bieber's* reagent suitable for the detection of all these adulterants ; as the quantitative reactions furnish ·greater certainty, the table of colour reactions given by *Tsujimoto* is not reproduced here.

Tsubaki oil is chiefly used as a hair oil. In the islands of Idzu it is used as an edible oil. Owing to its high price its industrial use is limited. It is also used as a lubricating oil for delicate machinery.

SASANQUA OIL [1]

French—*Huile de sasanqua.*   German—*Sasanquaol.*
Italian—*Olio di sasanqua.*

This oil is prepared from the seeds of *Thea sasanqua*, Nois (*Camellia sasanqua*, Thun [2]), a tree very similar to the tsubaki tree, and cultivated like the latter for ornamental purposes. The sasanqua seeds are smaller than those of tsubaki, their length varies from 1·0 to 1·5 cm. ; they weigh on an average 0·5 grms. The seeds consist of 28 per cent of husk, and 72 per cent of kernels. An analysis of the kernels gave the following result :—Moisture, 5·11-5·78 per cent ; oil, 58·1-59·4 per cent ; ash, 1·7-1·8 per cent.

The oil is prepared commercially in the prefecture Kumamoto by drying the seeds, powdering, steaming, and finally pressing in a wooden wedge-press. The powdered mass is generally expressed twice, so that 16 to 17 per cent of oil (by volume) are obtained.

· The examination of a cold pressed oil (from Amakusa seed) and an oil extracted with ether (from Tokyo seed) gave the following results :—

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[1] Tsujimoto, *Journ. Coll. Engin. Imp. Univ. Tokyo, Japan*, 1908, vol. IV. p. 80.
[2] A plant named *Camellia oleifera* grown in China appears to be of the same species as sasanqua.

	Cold pressed Oil.	Extracted Oil.
Oil—		
Specific gravity at 15° C. . .	0·9163	0·9188
Saponification value . . .	193·9	193·4
Iodine value	82·3	81·7
Reichert-Meissl value .	1·17[1]	
Refractive index at 20° C. . .	1·4691	1·4961[2]
Fatty Acids—		
Specific gravity at 100° C. (water		
at 15·5 = 1)	0·8405	
Melting point, ° C. . . .	28	
Neutralisation value . . .	199·64	
Mean molecular weight . .	281	
Iodine value	86·1	

The oil solidifies completely at − 9° C., in the elaïdin test it yields, after two hours, a hard mass. By the lead-salt-ether method 89·9 per cent of unsaturated acids (of the iodine value 92·9) were obtained ; as these yielded no insoluble bromides, the chief constituent fatty acid in sasanqua oil must be oleic acid.

Seeds from the Kwangsi Province (China [3]) yielded a yellowish brown slightly opalescent oil of the specific gravity 15·5°/15·5° C., 0·918 ; saponification value 193·4, and iodine value 87·5. The tea-seed cake from which this oil was obtained gave the following numbers :— Moisture, 8·83 per cent ; oil, 1·31 per cent ; crude proteins, 6·49 per cent ; ash, 3·2 per cent ; crude fibre, 37·3 per cent.

Sasanqua oil resembles tsubaki oil very closely. *Tsujimoto* is of the opinion that with *Bieber's* reagent this oil can be distinguished from tsubaki oil.

Sasanqua oil is chiefly used as a hair oil (as a substitute (?) for tsubaki oil). It is also employed as a lubricating oil.

INOY KERNEL OIL

This oil is obtained from the seeds of *Poga oleosa*, *Pierre* (a plant indigenous to West Africa [4]).

The tree bears a four-celled stone fruit having a fleshy exocarp and a thick wooden endocarp. Each cell contains one seed about 2 cm. long and 1 cm. in diameter. The shells form about 26 per cent of the whole fruit, the kernels (known to the natives of the Cameroons as " Njore-Njole," and in the Gaboon as " M'poga ") yield from 55 to 62

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[1] The high Reichert-Meissl value of this specimen is due to the high acid value, viz. 6·78.

[2] This figure should evidently be 1·4691.

[3] *Bull. Imp. Inst.*, 1912, 234.

[4] Cp. Pierre, *Bull. Soc. Linn. Par.*, 1896, ii. 1254. Pierre places the plant in the natural order *Phytolaccaceæ*. E. Drabble, *Quart. Journ. Inst. of Comm. Research in the Tropics*, 1908, 20, places the plant in the natural order *Rhizophoraceæ*.

per cent of a light yellow oil. The examination of the oil gave the
following numbers :—

		Oil extracted from Kernels.				
	Native Prepared Oil.[1]	I.[1]	II.[1]	III.[2]	IV.[3]	V.[4]
Oil—						
Specific gravity . .	0·918	0·896 (?)	0·914	0 9091	0·9135	0·9085
Solidifying point .	..	..	..	..	..	− 5
Saponification value	184·05	184·49	192 9	188·0	193 05	174·5
Iodine value . .	85·35	89·7	90·9	93·0	93·3	91·1
Refractive index at						
15° C. . . .	..	..	.	..	..	1·4700
Fatty Acids—						
Insoluble fatty acids						
+unsaponifiable .	..	93·0	94·5		.	95·83
Melting point, ° C. .	..	..	..	.		28·0
Titer test, ° C. . .	..	22	24·5			24·5
Iodine value .	.	.	..		.	93·6
Refractive index at						
45° C. . . .	..	..	.		..	1·4499

The specimen which the author obtained from the Imperial Institute,
deposited " stearine " on keeping.

PISTÁCHIO OIL [5]

French—*Huile de pistache.*   German—*Pistazienol.*
Italian—*Olio di pistacchio.*

This oil is contained in the seeds of the pistachio nuts (from *Pistacia
vera* or *P. lentiscus,* L.). Oil obtained by extraction with ether has a
more pronounced aromatic odour than that obtained by expression in
the cold.

Pistachio oil has very limited commercial application ; it is used
in the manufacture of sweetmeats.

[1] *Bull. Imp. Inst.,* 1906, 201 ; 1908, 358.
[2] Edie, *Quart. Journ. Inst. of Comm. Research in the Tropics,* 1907, 14.
[3] Brieger and Kranse, *Der Tropenpflanzer,* xii. p. 83.
[4] Grimme, *Chem. Revue,* 1910, 266.
[5] De Negri and Fabris, *Annali del Lab. Chim. delle Gabelle,* 1893, 220.

Physical and Chemical Characteristics of Pistachio Oil

Specific Gravity.	Solidifying Point.	Saponification Value.	Iodine Value.	Maumené Test.	Butyro-refractometer. "Degrees."
At 15° C.	°C.	Mgrms. KOH	Per cent.	°C.	At 25° C.
0·9185	−8 to −10	191·0-191·6	86·8-87 8[1]	44·5-45 [1]	62 [2]

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.	Solidifying Point.	Melting Point.	Iodine Value.
Per cent.	°O.	°C.	Per cent.
96·1 [1]	13 14-13	17-18 } 18-20 }	88·9 96·2 [2]

The seeds from *Pistacia terebinthus*, a small tree, native of the Mediterranean region, are known in commerce as "Hunnulk seed." (The bark of the tree yields a commercial Chian turpentine.) The oil contained in the kernels has not acquired commercial importance.

HAZELNUT OIL

French—*Huile de noisette.*   German—*Haselnussöl.*
Italian—*Olio di nocciuole.*

For tables of characteristics see p. 331.

Hazelnut oil is prepared from the seeds of the hazelnut tree, *Corylus avellana*, L., by pressing or by extracting with solvents. The seeds contain from 50 to 60 per cent of a golden-yellow coloured oil having the characteristic odour of hazelnuts, which assists to detect it in other oils.

According to *Hanus*,[3] the mixed fatty acids of hazelnut oil consists of 85 per cent of oleic acid, 9 per cent of palmitic acid, and 1 per cent of stearic acid. The iodine value of the liquid acids (*Tortelli and Ruggeri*) points, however, to the occurrence of linolic acid in hazelnut oil. *Fabris and Settimj*[4] found 80 per cent of liquid fatty acids in a specimen from dry hazelnuts which yielded 35 per cent of oil. In the elaïdin test hazelnut oil yields a solid white mass.

[1] De Negri and Fabris, *Annali del Lab. Chim. delle Gabelle*, 1893, 220.
[2] Fabris and Settimj. These observers give the iodine value 92·5 and Maumené test 55° C. for an oil obtained by expressing Sicilian seeds. The oil yielded 80 per cent of liquid fatty acids of the iodine value 105·8.
[3] *Chem. Zeit.*, 1899, Ref. 226.
[4] *Atti del VI. Cong. intern. di Chim. applic.*, Roma, 1907, vol. v. 755.

Physical and Chemical Characteristics of Hazelnut Oil

Specific Gravity		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Butyro-refractometer. "Degrees."	
At 15° C.	Observer.	°C.	Observer.	Mgrms KOH.	Observer.	Per cent	Observer.	°C.	Observer.	At 25° C.	Observer.
0·9170	De Negri and Fabris	−20	Girard	197·1	Filsinger	88	Girard	35-36	De Negri and Fabris	61·2	F. and S.
0·9169	Hanus	−10	Braconnot	192·8	De Negri and Fabris	86·2-86·8	De Negri and Fabris	36·2	Hanus		
0·9155	Fabris and Settimj	−18	F. and S.	193·7	Hanus	90·2	Hanus				
						83·9	Tortelli and Ruggeri				

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms KOH.	Observer.	Per cent.	Observer.
95·5	Schoettler	19-20	Schoettler	22-24	De Negri and Fabris	200·6	Hanus	90·1	De Negri and Fabris
95·6	Hanus			24-25	F. and S.			90·6	Hanus
								87·5	F. and S.
							Iodine Value of the Liquid Fatty Acids.		
								91·3	Hanus
								97·6	Tortelli and Ruggeri
								95·8	F. and S.

Hazelnut oil much resembles almond oil ; the lower iodine value and the lower solidifying point may serve as means to distinguish the two oils.

Hazelnut oil is used in perfumery, and as lubricating oil for watch springs and other delicate machinery.   It is also used in the adulteration of chocolate fats (*Filsinger*[1]) and as a substitute for peach kernel oil (*Bennett*[2]).   Hazelnut oil, in its turn, is liable to adulteration with olive oil ; the latter would be detected by the higher solidifying point of the sample.

" Giovani " nuts from *Corylus tubulosa* contain 56·04 per cent of oil (and 2·47 per cent nitrogen = 15·44 per cent protein[3]).

<div align="center">KOËME OIL [4]</div>

French—*Huile de Telfairia ; huile de noix d'Inhambane.*
German—*Koëmeöl, Thalerkürbisöl (Telfairıaol* [5]*).*
Italian—*Olio di telfairia ; olio di noce di Chilimanjaro.*

For tables of characteristics see p. 333.

This oil is obtained from the seeds of *Telfairia pedata*, Hook. fil. ; syn. *Joliffa africana*,[6] D.C., a tall climbing plant belonging to the *Cucurbitaceæ*, and indigenous to the Coast of South-East Africa and the islands off the East African Coast.   The fruit reaches a length of 2 to 3 feet and a breadth of 8 to 10 inches.   The fruits have internally three to six cells, each *loculus* containing a number of large, flat, almost circular seeds about $1\frac{1}{2}$ inches in diameter and $\frac{1}{4}$ inch thick.   The seeds are known in commerce as " Koëme de Zanzibar," " Kilima-Njaro nuts," [7] " Jacungu," " mkungu," and " limabu " nuts, and are largely used as an article of food by the natives.   The kernels have a pleasant taste, and do not easily become rancid even after keeping for several years, the shells apparently forming a good protection against .the influence of the atmosphere.   Specimens examined by the author yielded 60·5 per cent of oil.   Seeds examined by *Bontoux* [8] consisted of 46 per cent of shells and 54 per cent of kernels, yielding by extraction with carbon bisulphide 62·57 per cent of oil (calculated to the entire seeds 33·8 per cent).   By expression of the kernels on a laboratory scale *Bontoux* obtained 50 per cent of oil.   Both kinds of oil prepared by *Bontoux* have a yellowish-red colour.   According to *Drabble* [9] the

[1] *Journ. Soc. Chem. Ind.*, 1893, 5.
[2] *Chemist and Druggist*, 1908, 89.
[3] H. Kuhl, *Pharm. Zeit.*, 1909 (54), 58.
[4] Thoms, *Arch. d. Pharm.*, 1900 (238), 48.
[5] Cp. *Jahrbuch. d. Chem.*, 1899 (ix.), 354.
[6] This name is used for both *Telfairia pedata* and *T. occidentalis* ; the name *Joliffa africana* was first applied to *T. occidentalis.*
[7] Romaguoli, *L'Industria saponiera*, iii. No. 3.
[8] Unpublished observations.
[9] *Quart. Journ. of the Institute of Comm. Research in the Tropics*, 1907, vol. ii. No. 5, p. 135.

unshelled seeds contain 33-36 per cent of oil ; the shelled seeds yield 59 per cent.

The expressed oil has a pleasant and even sweet taste. Attempts to prepare an edible oil have hitherto failed owing to the difficulty of shelling the seeds by a cheap process. The removal of the shell must be carried out completely, as it has an extremely bitter taste, and may even give up toxic substances to the oil if expressed together with the pulp of the fruit (*Bontoux*).

The oil examined by the author had the acid value 0·56, and contained 0·9 per cent of unsaponifiable matter. It gave the elaïdin reaction ; on exposure to the atmosphere for several months it becomes slightly viscous.

The mixed fatty acids contain stearic, palmitic, and telfairic (Vol. I. p. 200) acids, and possibly an unsaturated hydroxylated acid of the composition $C_{24}H_{40}O_3$. The acetyl value of the oil, viz. 26·9, found by *Thoms*, is due to the presence of the hydroxylated acid. The low saponification value given by *Thoms* is open to doubt.

Physical and Chemical Characteristics of Koeme Oil

Specific Gravity.	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.	Refractive Index.		Observer.
At 15° C.	° C.	° C.	Mgrms. KOH.	Per cent.	Butyro-refractometer.		
					At ° C.	Scale Divisions.	
0·9180	+7	..	174·8 (?)	86·2			Thoms
					25	63·64	
					30	61·62	
			195·10	100·7	..	..	Lewkowitsch
			196 5 ;[1] 197·5[2]	88·5 ;[1] 88·3[2]	..	..	Bontoux
0·9185	+8·5	10	186·5	84·2	15	1·4686	Grimme

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Fatty Acids + Unsaponifiable.	Solidifying Point.	Melting Point.	Neutralisation Value.	Mean Molecular Weight.	Iodine Value.	Refractive Index at 50° C.	Observer.
Per cent.	° C.	° C.	Mgrms. KOH.				
	41	44					Thoms
	38·8						Lewkowitsch
	(Titer test)						
96·5	41·8	43·5	209·1	266	86·7	1·4492	Grimme

[1] Extracted oil.   [2] Expressed oil.

The seeds from *Telfairia occidentalis*,[1] Hook., known to the natives of the West Coast of Africa as " Krobonko " seeds, are very similar to those of *T. pedata*. They consist of 31·2 per cent of shells and 68·8 per cent of kernels. The kernels contain 48·2 per cent of oil, hence the whole seeds yield 32·2 per cent.

The oil obtained by extraction with ether had the following characteristics (*Grimme*) : [2]—

Oil—

Specific gravity at 50° C.	0·9135
Solidifying point, ° C.	− 2·5
Melting point, ° C.	− 1·0
Saponification value	262·2
Iodine value (*Wijs*)	43·4
Refractive index at 20° C.	1·4763

Fatty Acids—

Fatty acids, per cent	96·2
Unsaponifiable, per cent	0·38
Solidifying point, ° C.	39·5
Melting point, ° C.	42·0
Neutralisation value	221·0
Mean molecular weight	251·5
Iodine value (*Wijs*)	45·9
Refractive index at 50° C.	1·4613

ELDERBERRY OIL

French—*Huile de sureau*.   German—*Holunderbeerenol*.
Italian—*Olio di sambuco*.

This oil is obtained from the berries of the red elderberry, *Sambucus racemosa*.[3] A similar oil was prepared by *Byers and Hopkins* from the berries of *Sambucus racemosa arborescens*.[4]

[1] J. R. Jackson, *Chemist and Druggist*, 1906, No. 1.
[2] *Chem. Revue*, 1910, 268.
[3] Zellner, *Monatsh. f. Chem.*, 1902, 937.   *Journ. Soc. Chem. Ind.*, 1903, 101
[4] H. G. Byers and P. Hopkins, *Journ. Amer. Chem. Soc.*, 1902, 771.

Physical and Chemical Characteristics of Elderberry Oil

Specific Gravity		Solidifying Point		Melting Point		Saponification Value		Iodine Value		Reichert-Meissl Value		Refractive Index	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. 1/10 norm. KOH.	Observer.	At 20° C.	Observer.
0·9072	Byers and Hopkins	− 8	Byers and Hopkins	0	Byers and Hopkins	200·3	Byers and Hopkins	81·44	Byers and Hopkins	1·54	Byers and Hopkins	1·472	Zellner
0·9171	Zellner	−3 to −4	Zellner			196·8	Zellner	89·5	Zellner	1·8	Zellner		
								110·6	Lewko-witsch	1·3	Lewko-witsch		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Melting Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	°C	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
91·75	Byers and Hopkins	38	Byers and Hopkins	204·8	Zellner	93	Zellner
95·1	Zellner	43	Zellner			Liquid Fatty Acids.	
						120	Zellner

¹ This appears to be too high, in view of the Reichert-Meissl value found by the same observer.—(J. L.)

According to these authors the solid fatty acids consist exclusively of palmitic acid. *Zellner*, however, found, besides palmitic acid (the chief constituent), small amounts of arachidic acid. The liquid fatty acids form, according to *Byers and Hopkins*, 73·6 per cent of the mixed fatty acids, which agrees fairly well with 71 per cent found by *Zellner*. The distinct Reichert-Meissl value points to notable amounts of volatile fatty acids. *Byers and Hopkins* arrive at the following composition of the oil : palmitin, 22 per cent ; olein and linolin, 73·6 per cent (of which olein forms 92·2 and linolin 7·8), caprin, caproin, and caprylin, 3·0 per cent.

Zellner concludes from the iodine value of the liquid fatty acids, viz. 120, that about two-thirds consist of oleic acid and the remainder of linolic acid ; linolenic and isolinolenic acids could not be detected.

Zellner records the acetyl value 15·5, and the mean molecular weight of the acetylated acids (melting at 47°-49° C.) 286.

<center>ELOZY OIL</center>

<center>French—*Huile de citron de mer* ;[1] *huile d'Elozy.*   German—
Elozyol.   Italian—*Olio di Elozy.*</center>

This oil is obtained from the seeds of *Ximenia americana*, L. (*X. Russelliana*, Wall.), a tree belonging to the *Oleaceæ* and widely distributed over tropical America, Africa, Asia,[2] and the Pacific Islands. In the Gaboon (West Africa), the tree is known under the names " Elozy " and " Zégué " ; hence *Heckel* describes the oil under the name *Huile d'Elozy-Zégué*. At the West Coast of Africa the seeds are known as " Mpingi." In the catalogue of the Colonial section of the Paris Exhibition, 1879, the percentage of oil is given as 32·8. *Grimme*[3] found in a South American specimen 39·25 per cent of oil (63-82 per cent in the kernels, which formed 61·5 per cent of the fruits). This agrees with *Heckel's* earlier statement that the seeds consist of 60 per cent of kernels and 40 per cent of husks. The kernels yielded, on extraction with carbon bisulphide, 69 per cent of oil. *Suzzi*[4] found 65·6 per cent of oil in kernels from Serae, in Erythrea (Italian East Africa). The oil furnishes the following characteristics :—

[1] Heckel, *Les Graines grasses nouvelles ou peu connues des Colonies françaises*, Marseille, 1902, p. 27. *Der Pflanzer*, 1911 (7), 484.   [2] East India.
[3] Grimme, *Chem. Revue*, 1910, 157.
[4] *I Semi oleosi e gli olì*, published for the Milan Exhibition, 1906.

	Suzzi.	Grimme.	Schröder.[1]
Oil—			
Specific gravity at 15° C. .	0·9165	0·9248	0·9187-0·9220
Solidification point, ° C. .	+12 to +5	+2	+4
Saponification value . .	155·3 (?)	183·1	173·177
Iodine value	85·1	84·0	80-85
Maumené test, ° C. . . .	69	..	..
Unsaponifiable matter, per cent	2	2·91	0·5
Refractive index . . .	..	1·4737 at 20° C.	1·4677-1·4687 at 40° C.
Fatty Acids—			
Insoluble fatty acids+unsaponifiable, per cent . .	..	..	93·9-94·8
Solidifying point. ° C. . .	45·5-42	..	44·45
Melting point, ° C. . . .	45·5-48	51·52	49·5-50
Neutralisation value . .	171·3	172·3	..
Mean molecular weight . .	326·5	326	..
Iodine value . .	..	78·2	71
Refractive index at 60° C. .	..	1·4596	..

According to *Schröder* the fatty acids contain arachidic acid.

STAFF TREE OIL

French—*Huile de celastre.* German—*Celasterol.* Italian—
Olio di celastro.

This oil was prepared by *Suzzi* [2] from the seeds of *Celastrus Senegalensis,* which is widely distributed throughout Erythrea (Italian East Africa), where two species, viz. *C. Senegalensis* and *C. serratus,* occur. In the seeds collected in Hamasen *Suzzi* found 49·68 per cent of fatty matter with the following characteristics :—

Oil—

Specific gravity at 15°	.	.	.	0·9435
Solidifying point	.	.	.	– 3 to – 6° C.
Saponification value	.	.	.	223·5 (?)
Iodine value	.	.	.	86·7
Maumené test	.	.	.	77° C.

Fatty Acids—

Solidifying point	.	.	.	32·29° C.
Melting point	.	.	.	34·37° C.
Neutralisation value	.	.	.	188·7
Saponification value	.	.	.	189·2
Mean molecular weight	.	.	.	296·5

[1] *Arbb. d. Kaiserl. Gesundsh.,* 1911, 43.
[2] *I Semi oleosi e gli oli,* published for the Milan Exhibition, 1906.

The specimen of oil contained 10·12 per cent free fatty acids. The oil gives no colouration in the *Halphen* nor in the *Baudouin* test.

The seeds from the shrub *Celastrus paniculatus* yield a dark-red pungent oil from which " stearine " separates on standing   In Ceylon this oil is known as " Duhudu oil," and serves as a nerve stimulant ; it is also used there for external application to sores.

OLIVE OIL

French—*Huile d'olive.*   German —*Olivenöl.*   Italian –*Olio d' oliva.*

For tables of characteristics see pp. 340-342.

Olive oil is prepared from the fruits of the olive tree, *Olea europea sativa,* L.

The olive tree is most likely indigenous to Western Asia, but at an early date was introduced into all the countries bordering on the Mediterranean.   In Syria, especially in the neighbourhood of Aleppo and on Mount Lebanon, the olive tree is abundant, and has become completely naturalised in Greece, Italy, Spain, and the South of France. In Northern Africa, especially in Algeria and Tunis, the cultivation of the olive tree has again reached the considerable dimensions which it had in the times of the Roman empire, and later on in the tenth century, when even exportation of olive oil took place (cp. footnote 3, p. 343).   Recently the cultivation of the olive tree has been introduced into California, South Africa, and Australia.   The olive tree thrives best in a subtropical climate, and its successful cultivation extends in Europe as far north as latitude 44½°.   In America it scarcely extends to latitude 34°.

Attempts have been made in several parts of India to cultivate the olive, but although the tree grows well and flowers, the fruit seldom matures.

In Italy the young olive trees bear fruit two years after being planted, and after six years they become a source of income.   The cultivation requires great attention, not only as regards weeding, but especially as regards the prevention of diseases peculiar to the olive tree.   Noticeable amongst the diseases are the " pourridié," which affects the roots when they receive too much moisture, and " tuberculosis " (or " rogne ") caused by *Bacillus oleæ.*   The latter produces tumours which exhaust the tree and cause its death.   Fungi which especially attack olive trees are : *Fumago salici* and *Cycloconium oleaginum* (" occhio di pavone ").   The chief damage, however, is done to olives by insects, notably by the olive fly, *Mosca olivarum (mouche de l'olive),* also known as *Dacus oleæ.*   Other insects attacking the olive tree are several species of cochineal, such as *Lecanium* (large

cochineal), which assists the development of *Fumago salici*, "*Psylle de l'olivier*," *Aspidiotis nerii*, *Parlatoria calianthina*, and *Chilicorus*. For further information the reader must be referred to the papers mentioned in the footnote.[1]

With regard to the formation of the oil in the fruit see Vol. I. p. 1, and with regard to constituents of olive leaves and olive bark cp. *Power and Tutin*.[2]

The olives intended for oil production are gathered just before the period of maturity, as the oil obtained from the barely ripe fruit is much superior in quality to that obtained from fully ripe or over-ripe fruits.

The proportion of oil goes on increasing to the maximum found in the fruit which has reached complete maturity; it then decreases slowly. Ripe olives contain up to 70 per cent of oil. This figure is, however, an exceptional one, the fleshy part of the best cultivated olives containing only from 40 to 60 per cent of oil. The Algerian olives vary in their proportion of oil within wide limits, from 10·03 per cent (Tlemcen olives, demi-grosses, *Telsi*) to 32·98 per cent in the Jemmap olives, greffées, *Garel*.

More recent analyses of the most important kinds of Tunisian olives published by *Bertainchand*[3] are briefly summarised in the following table :—

Olives from				Yield of Oil.
Région du Nord				
Djebel Amar ⎫				
Tebowika ⎪				
Tunis ⎬	.	.	.	24·0-39·0
Zaghouan ⎭				
Région du Sahel				
Monastir ⎫				
Kalaa-Srira ⎭	.	.	.	28·3-41·0
Région du Sfax	.	.	.	32
Région de Gafsa				
Oasis de Gafsa	.	.	.	23·0-33·5
Région du Sud				
Oasis d'el Oudiana ⎫				
Gabès ⎪				
Djerba ⎬	.	.	.	22·5-49·0
Zarzis ⎭				

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[1] Cp. *Rapport sur les cultures fruitières, et en particulier sur la culture de l'olivier*, Tunis, 1899 ; *Congrès oléicole et concours régional agricole de Sfax*, 18 et 25 janvier 1904, Tunis, 1904 ; J. Dugast, *L'Industrie oléicole (Encyclopédie scientifique)*; L. Trabut et R. Marès, *L'Algérie agricole en 1906* (Olivier, pp. 186-230) ; Alger, 1906 ; *Olives* ; *Varieties and their Adaptation*, by George E. Colby (Bulletin No. 123) ; *Revision of Report on the Condition of Olive Culture in California*, by A. P. Hayne (Bulletin No. 129) ; *California Olive Oil, Its Manufacture*, by G. W. Shaw (Bulletin No. 158) ; *L'Exportation des huiles d'olive tunisiennes en Angleterre*, J. Simonot, Tunis, 1909 ; "Die Ölproduktion am der italienischen und französischen Riviera" : J. Slaus-Kantschieder, *Zeitschr. f. landw. Versuchsst.*, 1909.

[2] *Proc. Chem. Soc.*, 1908, 117.

[3] Dugast, *L'Industrie oléicole*, Paris, 1905.

Physical and Chemical Characteristics of Olive Oil

Specific Gravity			Solidifying Point		Saponification Value		Iodine Value		Reichert Value	
At °C.		Observer	°C.	Observer	Mgrms. KOH	Observer	Per cent.	Observer	c.c. 1/10 norm. KOH	Observer
15	0·9178 [1]	Clarke	At 2 turbid, at −6, "stearine" separates +3 to +4 [8]	Chateau	191-196	Allen	82·8	Huhl	0·3	Medicus and Scheerer
15	0·9196 [2]				188·7-203 [1]	Dieterich	81·6-84·5 [1]	Dieterich		
15	0·916-0·918 [3]	De Negri and Fabris			185-196 [3]	De Negri and Fabris	79·18-82·3	Villavecha		
							79·88 [3]	De Negri and Fabris		
15·5	0·91747-0·91797 [4]	Moerok	+9 to +10 [9]	Bertainchand	generally 190	Oliveri	generally 82	Oliveri		
							79·83 [10]		Reichert-Meissl Value	
15·5 (water at 15·5 =1)	0·9203	Crossley and Le Sueur [5]	,,		190·5-195 [10]	Crossley and Le Sueur [5]	78·9-86·9	Thomson and Ballantyne	0·6	Crossley and Le Sueur [5]
					190·9 [5]		77·28-88·68 [4]	Lengfeld and Paparelli		
15·5	0·9155-0·9180 [6]	Tolman and Munson			189·3-194·6 [4]	Tolman and Munson	80·7-91·5 [11]	Gnozlenović		
							83·3-86·1 [12]	Ferreira da Silva		
15·5	0·9162-0·9180 [7]	Stilurell					93·67 [5]	Crossley and Le Sueur		
18	0·9144-0·9163	Long					78·6-87·2 [13]	Tortelli and Ruggeri		
18	0·9139-0·9141	,,								
19	0·9134	,,					84·0 [14]			
19	0·9127	,,					79·1 [15]			
20	0·9119-0·9121	,,					87-87·5 [16]	Ahrens & Hett		
21	0·9112-0·9114	,,					91·4-91·7 [17]	Tolman and Munson		
22	0·9106-0·9117	,,					85·1 [4]			
23	0·9101-0·9099	,,								
24	0·9094	,,					81·5 [18]	Thomson and Dunlop		
25	0·9060	,,					94·3 [19]			
30	0·9028	,,								
35	0·8932	Saussure					82·8 [20]	Shukoff		
50	0·8625	,,					85·21			
94		,,					82·4-94·7 [22]	Archbutt		
							82·4-90·4 [23]	,,		

[1] "Virgin oil."
[2] Gallipoli oil.
[3] Derived from observations on 203 samples.
[4] Californian oils.
[5] Oil from the Punjab.
[6] 18 Italian oils.
[7] 38 Californian oils.
[8] Tunisian oils from the South (Gatès, Safsa, Djerba)

[9] Tunisian oil from Sfax (cp. pp. 739 and 753).
[10] Derived from observations on 106 samples
[11] 60 samples of Dalmatian oils (in one case 92·8 was found)
[12] Portuguese oils.
[13] Spanish oils.
[14] Greek oil.
[15] Turkish oil.
[16] Morocco oil from green olives (*Chem. Zeit.*, 1903, 241).

[17] Morocco oil from black olives.
[18] Italian oils.
[19] Mogador oil : this oil possibly contained, or consisted entirely of, "Argan Oil."
[20] Crimean oil.
[21] Persian oil.
[22] Tunisian oils.
[23] Algerian oils.

Physical and Chemical Characteristics of Olive Oil—continued

Thermal Tests.

Maumené Test		Heat of Bromination.		Specific Temperature Reaction.	
°C	Observer.	°C.	Observer.	°C	Observer.
41·5-45·5	Archbutt	15	Hehner and Mitchell	89-95	Thomson and Ballantyne
35·3, (mean)	De Negri and Fabris	14·3	Jenkins		
45-47[4]	Blasdale	13·55 to 14·5	Archbutt		
44[8]	Tortelli				

Refractive Index.

At °C	Refractive Index.	Observer.
15	1·4698	Strohmer
15	1·4703[5]	Guozlenovð
15·5	1·4703·	Tolman and Munson
20	1·4713[4]· 1·4670-	Holde
60	1·4705 1·4518	Thorner

Oleo-refractometer

"Degrees."	Observer
0 to 2	Jean
0 to +1 5	Bruyn and van Leent
+1 to +3·5[6] at 22° C	Peatman

Butyro-refractometer.

At °C	"Degrees."	Observer.
15·5	67·3-68·5[7]	Tolman and Munson
15·5	66·9-69·2[4]	Mansfeld
25	62·62·8	Bomer
40	54·13-54·7	Crossley and Le Sueur
40	56·4[1]	

Viscosity in Redwood's Viscosimeter.

Seconds at 70° F.	Observer.
312·3[1]	Crossley and Le Sueur

[1] Oil from the Punjab.   [2] Derived from observations on 203 samples.   [3] By Jean's thermoleometer.   [4] Californian oils.
[5] 60 samples of Dalmatian oils (in one case the iodine value was 92·8).   [6] 105 samples.   [7] Italian oils.   [8] Tortelli's thermoleometer.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	At ° C.	Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At ° C.	Observer.
94·96 6	Lengfeld and Paparelli	0·8430 99 (water 15·5=1)	Allen	21	Allen	26	Allen	193	Thorner	279·4	Allen	86·1	Morawski and Demski	40 1·4528	W. B. Smith
95·14 1	Crossley and Le Sueur	0·8749 100 (water 100=1)	Arch-butt	Not below 22 · 23·5-24 6 · 22·17 2	Bach · Dieterich · De Negri and Fabris	23·24 to 26·27 · 26·5-28·5 · 24·27·5	Bense-mann Bach · De Negri and Fabris			286	Williams	90·2 · 87·88	Williams · Thorner	60 1·4410	Thorner

Titer Test.

		Lewko-witsch	16·0-17·15	19·23·6 Mostly below 28·6	Moerk		Iodine Value of the Liquid Fatty Acids.
			17·1-17·8 3	21·26·6	Lengfeld and Fabris		
			18·6-19·7	21·6-29·3 8	Paparelli Thorner Blasdale 7		
			19·45-20	19·2-31·0·6	Tolman and Munson	96·4-97 · 92·8 6	Bömer · Tolman and Munson
			23·25 4			94·0 8	
			20·1-21·2			95·5-	
			19·75-20·8			101·5·9	Tortelli and Ruggeri
			21·2-21·87			95·5- · 104·2 10	
			21·5-22·9			103·5 11	
			18·4-19·2			96·3 12	
			18·9-19·8			95·5-	
			25·2-26·4 5			112 13	Bertainchand

Refractive Index of the Liquid Fatty Acids. — Butyro-refractometer.

At 40° C.	Observer.
42·7	Bömer

1 Oil from the Punjab.   2 Derived from observations on 203 samples.   3 Finest Tuscan cream.   4 Commercial oil.   5 Gallipoli oil.   6 Californian oils.
7 Journ. Soc. Chem. Ind., 1896, 206.   8 Italian oils.   9 12 Italian oils, iodine values varied from 80·0 to 85·4.   10 7 Spanish oils, iodine values varied from 78·6 to 87·2.
11 Greek oil, iodine value 94·0.   12 Turkish oil, iodine value 79·1.   13 Tunisian oils; cp. p. 363.

The Tunisian oils may be classed broadly into three groups : (1) Oils of the North, (2) Oils of the Centre, and (3) Oils of the South of Tunis. Of course, this classification must not be taken in too strict a sense, for in each part of the country different types of oils are found, the composition of which depends on the variety of the olive tree, on the state of ripeness, etc. The oils from the North of Tunis (Tebourba, Bizerte, and Cap Bon) have as a rule a fruity, slightly pungent taste. The oils from the South (Sfax) have a full very delicate taste. Those of the Centre of Tunis (Sousse, Monastir, Mahdia) represent an intermediate type.[1] (For analytical characteristics see p. 363.)

Californian olives also yield much smaller quantities of oil than the best-cultivated European varieties. Among the large number of analyses published by the Agricultural Experiment Station of the University of California the lowest percentage of oil was 11·23 (in the locality of Sacramento), and the highest, 22·3 (in Oakdale); both olives are varieties of the " mission " olive, the oldest olive grown in the State. The " ruabra " olive imported into California from France yields up to 27·91 per cent (district of Lincoln).

When determining the proportion of oil in olives or olive pulp, carbon bisulphide should be used in preference to ether, as the latter dissolves other (non-fatty) substances together with the oil.[2]

The technical processes employed for the production of olive oil furnish one of the best examples of the correctness of the statement made at the beginning of Chap. XIII. The very oldest and crudest processes still survive in those districts of Algeria and Tunis[3] which are farthest removed from the coast. The difficulty which especially besets the production of olive oil is the feature that it is impossible to gather all the fruit at the most favourable time and crush it immediately. Hence the fruit must be preserved until it can be worked up ; otherwise, fermentation, with subsequent hydrolysis and oxidation of the oil, sets in (see below). Many methods have been proposed for preserving the fruits ; the best seems to be storage in well-ventilated rooms, the olives being exposed to the air in shallow layers. Where

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[1] Simonot, L'Exportation des huiles d'olive tunisiennes en Angleterre, p. 14.

[2] Cp. Peano, Journ. Soc. Chem. Ind., 1903, 35.

[3] The culture of the olive tree in Tunis dates from about the first century B.C. It was very prosperous until the sixth invasion of the Arabs (693-694 A.D.), who destroyed a great number of plantations. During a later invasion of the Arabs in 1048 the olive trees of the Sfax district were entirely destroyed. Fresh plantations were not made before 1800-1810. Since then the olive culture has developed greatly, so that the number of olive trees in Tunis was estimated, in 1908, at 11,222,525. In the Sfax district, the most important and progressive in Tunis, two kinds of olives are planted for eating purposes : (1) the "mellah," a round fruit reaching sometimes the size of a small apricot, which is picked green for salting ; and (2) the "nab," which is smaller than the former and has an oval shape. The olives grown for oil production are of the "chemlali" type. This fruit, which is much smaller than the "mellah" and "nab," grows over the whole of North Africa. Two-thirds of the oil produced in Tunis comes from Arab mills, where the most rudimentary processes still survive, the "mill" being merely a roller turning inside a cylindrical basin ; the roller is driven by animal power. The fruits and stones reduced to a pulp are spread over round pieces of matting made of esparto grass which are put into a wooden press when a mixture of water and oil exudes. If the olives cannot be worked up immediately, they are placed in a dark room and each layer of olives is covered with salt.

this is not possible, recourse is had to preservation in sea-water or brine, with exclusion of air.[1] Storage in refrigerated chambers would undoubtedly be better,[2] but this may be too expensive.

In this work only the most modern methods adapted to large scale operations can be considered. They consist in working up the olives by the mixed process (p. 29), *i.e.* by expression and subsequent extraction. Therefore, reference can only be made in passing to processes such as those proposed by *Kuess*,[3] *Funaro*,[4] *Tanquerel*,[5] *Miguel del Prado*,[6] *Acuña y Gomez de la Torre*,[7] *Acapulco*,[8] *Sagols*,[9] *G. Quintanilla*,[10] and *J. Bernardini*[11] (cp. above p. 2).

The machinery employed in the production of olive oil varies considerably in the different countries, although in the main it is of the same kind as that described in broad outlines in Chap. XIII. For a description of the special apparatus employed in Tunis and California (adapted from the methods worked in France and Italy), the reader must be referred to the special work by *Dugast* and the " Bulletins " published by the *Agricultural College of the University of California.* It may suffice here to give in a general way an account of an ideal process producing all kinds of olive oil from the very finest down to the very lowest, and embracing the various methods in vogue in the different countries.

The very finest oils are obtained from *hand-picked fruits*[12] by first crushing them in a mill without breaking the kernels. Exceptionally fine qualities are prepared by peeling hand-picked fruits and pressing lightly, after carefully removing the kernels. The crushed mare is then expressed in a hydraulic press ; the oil so obtained ranks as the best edible oil—*huile vierge, huile surfine.*[13] Commercial brands of this quality are " Provence Oil," " Aix Oil," " Nice Oil," " Var Oil." The oils sold as " Finest Tuscan Cream," " Riviera Oils " (Genoa), " Bari Oils " also rank amongst the best edible oils, although they are distinctly lower in value than the South of France oils, and approximate more closely to the following somewhat inferior quality. The latter is obtained by pouring some cold water on the marc, after the pressure

[1] Klein, *Zeitschr. f. angew. Chemie*, 1898, 848 ; Mastbaum, *Chem. Revue*, 1904, No. 345.

[2] Cp. G. Sani, *Atti R. Accad. dei Lincei*, Roma, 1912 (21), 364 ; cp. also O. Klein, *Chem. Zentralbl.*, 1912 (I.), 1664.

[3] French patent 291,559, 1899.   [4] *Staz. esper. agrar ital.*, 1902, p. 916.

[5] French patent 345,849   [6] French patent 365,187, 1906.

[7] French patent 403,015.

[8] Cp. Bertainchand's "Report" at the Congrès Oléicole, Avignon, 1912. (The process is also known as the Acapulco-Mingioh process) ; cp. also *Les Matières grasses*, 1913, 3011.   [9] French patent 411,943.

[10] French patent 419,207.   [11] French patent 431,351.

[12] The method of knocking off the fruits by poles leads to bruising of the olives ; such damaged olives furnish an inferior oil.

[13] Marcille (*Bulletin de la Direction de l'Agriculture du Commerce et de la Colonisation*, Tunis, 1907, 531) points out that the epidermis of olives is richer in vegetable acids, has a harsher taste, and contains larger amounts of tanning and ethereal substances than the marc. He further showed that these foreign substances pass to a greater extent into the olive oil, if the pulp is more thoroughly broken up and the pressure higher than in the case of peeled olives. The superiority of the "virgin oil" is therefore easily explained and does not seem to be conditioned by the removal of the kernels.

in the hydraulic press has been released, and pressing again. Such inferior oil is also sold as an edible oil either alone or after admixture with the oil of the first expression—" Salad Oil," *huile fine, huile de table ordinaire.*

The pulp is now taken out of the press, mixed with *hot* water, and pressed again *once* or *twice*. Thus the bright oils used for various technical purposes—*huile de commerce, huile d'industrie, huile échaudée* —are obtained. They are especially used for lubricating purposes, as burning oils, and for soapmaking, under the following names : *huile lampante, huile à brûler, huile à fabrique* ; *olii lavate* (washed oils).

All the oils obtained so far are somewhat turbid and must therefore be brightened by washing and filtering.[1] In the case of the edible oils settling and subsequent filtration suffice for the production of merchant-able oils. Most of the technical oils are treated in the same way ; oils of lower qualities are refined in the same manner as rape oil, *i.e.* by treatment with sulphuric acid.

In the majority of the smaller works the kernels are not removed and are crushed together with the fruit. In large establishments, however, the kernels are removed and crushed separately, yielding the olive kernel oil, described p. 367. Opinions, however, differ as to the advantage this procedure is said to offer. At any rate for lower class edible oils the removal of the kernels seems to make no difference in the quality of the oil.[2]

The repeatedly pressed pulp—grignons (*bucchiette, polpè*)—still contains a considerable amount of oil, varying in a number of samples examined by the author from 10 to 22 per cent. The pulp is now beaten with hot water in special mills—*moulins de ressence*—resembling the well-known edge-runners. The oil cells are thereby further broken up ; the ground mass, together with the water, is then allowed to run into a series of vessels, arranged in tiers, where the water separates from the oil and broken cellular tissues. The oil and the tissue rise to the surface, when they are skimmed off, whilst the heavier crushed kernels fall to the bottom. The latter are known as *grignon marc blanc.* The emulsion of oil and cellular tissue, which has been skimmed off the water, and is known as *grignon marc noir*, is heated and subjected to a fresh expression in a hydraulic press. The oil so obtained is termed *huile de ressence*, and the pressed residue is known as *tourteau de ressence.* The *huile de ressence* is allowed to rest in large tanks at a somewhat elevated temperature, when a clear oil separates on the top—*huile claire de ressence*—and a lower layer of thicker oil—" Olive Oil Grease "—*pâte de ressence*—settles out. Such an " olive oil grease " examined in the author's laboratory contained 48 per cent of free fatty acids. In consequence of the repeated treatments, this oil has

[1] A special apparatus for washing olive oil has been patented by V. Coq, French patent 360,733, 21st December 1905.

[2] Cp. Passerini, *Staz. sperim. agr. italiani*, 1904 (37), 600. Marcille (*Bulletin de la Direction de l'Agriculture du Commerce et de la Colonisation*, 1907) discusses this subject exhaustively, and shows that the previous separation of the kernels from the pulp is an unnecessary operation and only leads to higher working costs.

become oxidised to some extent. A specimen of *pâte de ressence* examined by *Merklen* [1] contained about 10 per cent of lactones.

In some establishments the marc, instead of being boiled with water, is thrown into pits where the pulp undergoes a kind of fermentation (see below under "Free Fatty Acids"), whereby the oil is set free and gradually rises to the top. Oil of this kind is known as *huile d'enfer, huile d'infect, Nachmühlenöl, Höllenöl, Sottochiari*. The name *huile d'enfer* is applied also to oil settled out from the waters obtained from the press after moistening and boiling the pulp, which has been stored in underground cisterns, "*enfers.*" To this class of oils belong the *bagassa (bagasse)* oils, which are obtained from fermented marc, principally in Portugal. These oils contain as much as 60-70 per cent of free fatty acids.

"*Tournant oil*" is a commercial product of the quality of the "*huiles d'enfer,*" obtained from the fermented marc of expressed olives; it contains a considerable quantity (up to 26 per cent) of free fatty acids, and, therefore, forms a very complete emulsion with a solution of sodium carbonate, which constitutes its value as Turkey-red oil (Chap. XV.). It was first employed for this purpose by *Haussmann* in 1792, and again recommended by *Koechlin Frères* in 1811.

The cake remaining after the removal of the *huile de ressence*, termed *tourteau de ressence*, or *sanza*, is finally deprived of its last content of oil by extracting with solvents, sometimes after a preliminary drying. The solvent most usually employed in France and Italy is carbon bisulphide. Hence, these oils are termed sulphocarbon oils, sulphur olive oils, *huiles de pulpes d'olive sulfurées, huiles de pulpes d'olive, huiles d'olive sulfurées; Sulfurole*. They have a deep green colour, due to chlorophyll extracted by the solvent, and contain the more solid portion of olive oil which has remained in the pulp. The proportion of lactones in these low-class oils is, however, small, due to the slight solubility of lactones in carbon bisulphide (or petroleum ether). *Merklen* [2] states that sulphur oils contain as a maximum 1 per cent of lactones. Some such sulphur oils (Italian and Syrian) examined by the author (Vol. I. Chap. V.) contained from 48 to 64 per cent of free fatty acids. These oils are characterised by the presence of organic sulphur compounds. (For the detection of sulphur see Vol. I. Chap. IV.) For the bleaching of such oils by means of organic peroxides cp. French patent 378,515 (*Vereinigte Chemische Werke, Charlottenburg*).

Suggestions have been recently made aiming at the extraction of the *sanza* with carbon tetrachloride,[3] or trichloro-ethylene (p. 24); these solvents cannot compete with the cheaper carbon bisulphide.

Instead of extracting with carbon bisulphide, *Rodolphe Bernard* proposes to treat the intimate mixture of pulp and water—*crasse d'huile d'olive*—with concentrated sulphuric acid in order to break

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[1] *Études sur la constitution des savons de commerce*, Marseille, 1906, p. 106.

[2] *Ibid.* p. 10.

[3] Cp. P. Bernard, French patent 338,354; cp. also Vol. III. Chap. XVI. A description of the process and a calculation of cost had been given by R. Jurgensen (*Zeitschr. f. angew. Chem.*, 1906, 1546), who curiously enough states that the apparatus is made entirely of iron, and is not attacked by carbon tetrachloride.

the emulsion.[1] This method cannot compete with the extraction process.

The water—*eau de végétation*—which collects in the pits after decantation of the supernatant oil is a black acid liquid known as "margines," *agua ruça*. The specific gravity varies from 1·050 to 1·060. It contains small amounts of nitrogenous substances, potash salts, and other extractive substances from the flesh of the olive. Hitherto this liquid has not been worked up commercially, not even for the recovery of the potash it contains.[2]

The extracted cake is sold as manure. The press residues, which have yielded superior kinds of olive oil, would be suitable for feeding cattle, but as the oil which can be easily recovered by extraction— about ten per cent of the residues—is too valuable, olive cakes are only used locally and to an inconsiderable extent. Moreover, consider-able quantities of nitrogenous substances and potash salts are lost to the cakes by having passed into the "margines"[3] (see above). The olive cakes become so rapidly rancid that they would have to be used up in the fresh state. Still, small quantities of the pressed residues are fed locally to pigs. *Miguel del Prado* in his above-mentioned French patent 365,187 especially claims the production of feeding cakes.[4]

Various proposals have been made to work up the extracted olive oil residues by destructive distillation (*Jürgensen*[5]). *Guerrero de Smirnoff*[6] took out a patent for working up the residues for char (carbon) on the one hand and ammoniacal salts, acetates, methylalcohol, etc., on the other hand, by a process of dry distillation.[7]

The commercial importance in the Mediterranean of olive oil may be gathered from the following table :—

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[1] French patent 325,966.

[2] Cp. *Les Huiles d'olives de Tunisie et l'utilisation des margines*, E. Millau, Bertain-chand, et F. Malet, *Moniteur scientifique*, 1900, 508 ; E Millau, *Bullet. de la Direction de l'Agriculture et de la Commerce*, Tunis, 1903, p. 488.

[3] Cp. O. Klein, *Zeitschr. f. angew. Chem.*, 1900, 635.

[4] Cp. also M. Hieguet and A. Bengesco, French patent 372,782.

[5] Paris Congress of Applied Chemistry, 1900.

[6] French patent 353,970, 1905. Cp. also Marchette and Molco, *Chem Zeit.*, 1906 972.

[7] T. Mancini, *Staz. sperim. agrar. ital.* 42, 553. Cp. also French patents 399,341 and 399,342 of *Las Industrias del olivo*.

Mean [1] *Production of Olive Oil during* 1900 *to* 1906 *in the*
Mediterranean Basin [2]

	Hectolitres.
Spain	2,660,000
Italy	2,604,330
Asiatic Turkey . .	1,980,000
Greece [3] . . .	601,411
Portugal . . .	398,150
France	333,000
Tunis	301,100
Algeria . . .	231,000
Austria . .	65,366

9,174,357, or about 820,000 tons.

It will be seen from the above table that France produces a comparatively small amount of olive oil. Large quantities, however, are imported, especially from Algeria and Tunis,[4] to be mixed with home-grown oil, a portion of which is again exported. The following table gives the French imports and exports of olive oil during 1900–1911 :—

[1] The *mean* production is given, as the production varies within very wide limits from year to year, the conditions of weather, ravages by insects, etc., influencing the harvest to an extremely large degree.

[2] Statistics of the French Ministry of Agriculture.

[3] For a report on the production of olive oil in Crete cp. *Zeitschr. f. angew. Chem.*, 1907, 1917.

[4] The exports of olive oil from Tunis during 1902–1907 were as follows :—

To	1902.	1903.	1904.	1905.	1906.	1907.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
France . .	3,547	5,874	11,312	6,386	8,591	11,937
Algeria .	43	59	189	73	214	524
Other countries .	538	261	2,275	2,862	2,466	3,580
Total . .	4,128	4,194	13,776	9,321	11,271	16,041

Olive Oil Imports into, and Exports from France

Double (metric) hundredweights.

	1900.	1901.	1902.	1903.	1904.	1905.	1906.	1907.	1908.	1909.	1910.	1911.
Imports—												
" Commerce général "	276,238	285,937	380,515	295,887	471,859	282,180	410,257	319,237	492,149	225,095	439,536	232,923
" Commerce spécial "	167,234	170,825	200,141	181,120	205,024	187,045	252,632	213,587	305,693	110,388	253,759	129,076
Exports—												
" Commerce général "	170,026	187,830	171,766	172,480	193,968	219,963	228,198	218,582	221,652	194,679	200,061	167,428
" Commerce spécial "	66,020	72,597	43,952	46,563	53,959	78,600	95,936	97,782	67,992	75,404	52,441	50,403

The exports of " refined " olive oil and of all other grades from Italy for the years 1905–1911 are given by the Italian Customs authorities as follows :—

Italian Exports of " Refined " Olive Oil

Exported to	Quintals.[1]						
	1905.	1906	1907.	1908.	1909.	1910.	1911.
United States .	38,687	71,400	29,188	23,477	20,106	42,397	44,479
Austria-Hungary	7,752	22,203	28,908	6,730	6,936	21,633	15,911
Germany . .	5,490	11,132	15,690	9,591	3,348	10,013	7,762
Great Britain .	4,102	9,432	5,861	2,525	4,295	4,656	6,573
Holland .	8,403	23,519	12,648	12,327	3,695	9,323	13,863
Switzerland	6,936	11,294	7,626	8,924	2,038	12,576	5,981
Egypt . .	4,867	19,285	15,353	3,855	8,788	20,765	16,214
Other countries	4,900	8,894	8,536	9,751	6,342	6,103	5,808
Totals . .	81,237	177,259	113,890	75,189	55,728	127,466	115,591

Italian Exports of all other Grades of Olive Oil

Exported to	Quintals.[1]						
	1905.	1906.	1907.	1908.	1909.	1910.	1911.
Austria-Hungary	18,293	25,834	19,013	17,784	6,258	9,330	7,274
France . .	43,191	116,312	60,766	44,974	21,794	40,291	33,643
Germany . .	11,058	21,222	17,793	8,490	3,928	5,577	3,735
Great Britain .	22,184	29,737	25,000	18,991	11,521	16,471	13,103
Russia . .	29,765	22,854	26,677	8,319	10,903	4,049	2,992
Switzerland	5,668	8,819	7,124	5,459	1,682	2,493	2,031
Egypt . .	1,956	5,810	2,636	2,136	1,289	1,991	889
United States .	52,577	95,258	82,198	91,798	62,224	96,040	93,096
Brazil . .	8,820	12,320	14,495	12,950	6,730	15,862	11,873
Argentina . .	58,256	109,194	90,347	127,115	47,507	73,534	59,981
Uruguay . .	3,893	8,190	9,402	7,428	1,797	3,421	2,950
Other countries	17,440	33,032	32,976	10,461	25,060	16,205	17,103
Totals . .	273,101	488,582	388,427	355,905	206,693	285,164	248,670

The imports of olive oil into the United Kingdom (chiefly from Italy, Spain, and France) are given in the following table :—

Year.			Tons.	Year.			Tons.
1866 .	.	.	16,935	1906 .	.	.	14,386
1870 .	.	.	23,202	1907 .	.	.	12,328
1875 .	.	.	35,453	1908 (unrefined)		.	6,330
1880 .	.	.	20,260	1908 (refined) .		.	5,822
1885 .	. .	.	24,227	1909 (unrefined)		.	4,788
1890 .	.	.	20,187	1909 (refined)		.	4,186
1895 .	.	.	14,834	1910 (unrefined)		.	6,905
1900 .	.	.	12,044	1910 (refined)		.	6,311
1902 .	.	.	18,978	1911 (unrefined)		.	4,424
1903 .	.	.	14,485	1911 (refined)		.	4,336
1904 .	.	.	15,010	1912 (unrefined)		.	9,611
1905 .	.	.	12,042	1912 (refined)		.	6,686

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[1] 1 quintal = 220·46 lb.

Some details as to the exporting countries are contained in the following table :—

Olive Oil imported into the United Kingdom (in metric tons)

From	1902.	1903.	1904	1905.	1906	1907.	1908.	1909.	1910	1911	1912.
Algeria .				7	0 8						
Italy	4,617	2,684	2,880	2,820	4,798		1,796	1,196	1,754	1,357	1,480
Spain	11,973	9,543	9,928	4,043	228		726	845	1,761	827	2,009
France	1,482	1,213	1,324	1,422	2,348		2,085	1,491	1,621	1,119	1,664
Greece .	639	112	307	114	992		428	71	481	234	785
Crete .		277	251	537	2,812		131	110	319	96	43
Tunis .						15					

Owing to the ravages of the olive fly (and in latter years owing to the introduction of other edible fats and oils) the production of olive oil in Italy has decreased, and olive oil has been imported in growing quantities from Greece, Spain, and Austria-Hungary. Whereas the import of olive oil during the years 1905–1909 amounted to 51,000 quintals only, it had risen in 1910 (when the harvest was bad) to 58,000 quintals (other edible oils which were imported during 1905–1909 to the extent of 172,000 quintals had risen in 1910 to 311,000 quintals).

The German imports of olive oil are given in the following table :—

Imports

From	1911.	1912.
	Tons.	Tons.
France .	933	1,476
Greece .	224	434
Italy .	1,116	1,799
Spain .	57	435
Turkey .	66	116

In the Southern Caucasus the production of high-class olive oils has been taken in hand. The olive oil produced there represents two distinct varieties, of different taste and colour. They are known as " Artwin " and " Barku " olive oils.

As regards California, in the year 1899 two and a half million olive trees were counted, which were judged to be able to furnish over two million gallons of oil, not counting the olives required for preserving. This quantity has, however, not been produced,[1] as the consumption of olive oil in the United States of America is covered to the greatest extent by the importation of olive oil from France, Italy, and Spain ; smaller quantities are imported from Greece, Portugal, and Austria. The products of the last three countries are not only cheaper—notwithstanding import duty—but are also preferred on account of their flavour ; for most of the oil produced in California has still a harsh flavour. This difficulty militates against the more rapid expansion of

[1] The maximum amount of olive oil produced is stated not to have exceeded 500,800 gallons.

the industry at present, but it is hoped that it will be overcome by the great efforts being made by the olive growers under the ægis of the *Agricultural Experiment Station of the University of California.*

The production of oil in South Australia is also increasing rapidly. Whilst in 1901, 6520 gallons only were produced, the Colony possessed in 1902, 66,852 olive trees yielding 11,327 gallons of oil. In 1907 the number of olive trees was 83,513, and the oil obtained per annum amounted to 15,000-18,000 gallons. The samples of olive oil shown at the Franco-British Exhibition of 1909 were practically neutral and had an agreeable taste.

From the above sketch of the processes employed for the production of olive oil it will be readily gathered that the specimens found in commerce must vary to a considerable extent, their quality depending on many circumstances, such as the variety of the olive tree itself (Italy alone produces about 300 varieties of the olive), the climatic conditions, the nature of the soil, the degree of ripeness of the fruit, the manner of gathering it, the mode of expressing, etc. The value of the edible oils in particular depends on their limpidity, colour, and especially on their taste.

Limpidity is one of the chief properties a good edible oil should possess. This is, in the first instance, obtained by proper filtering and then by allowing the oil to deposit all the " stearine " that will settle out at such temperatures as the oil is required to withstand. An oil which will remain clear at 10° C. will always command a higher price than an oil which becomes turbid or even sets to a pasty mass at this temperature.

The **colour** of olive oil varies considerably ; the commercial oils represent all shades from water-white to golden-yellow ; a green colour, which is very pronounced in low-class olive oils, is due to dissolved chlorophyll.

The **taste** of purest olive oil is bland and pleasant ; it varies, however, with the locality where the fruit has been grown. Thus, the oils obtained from Tuscan fruits possess a decidedly more agreeable taste than those from Ligurian olives. Much also depends on the degree of ripeness of the fruits at the time of gathering. Therefore purity alone is not a sufficient test in the valuation of a sample of edible olive oil. An oil may be free from adulteration and still be an inferior oil, on account of its harsh or rank or even nauseous taste. *Canzoneri* [1] isolated from the bitter and harsh Puglia olive oils eugenol, to which he ascribes the harsh taste ; and further catechol, gallic acid, tannin, and an unknown substance, all of which are said to cause the bitter taste. It is noteworthy that the objectionable taste disappears in time. The large quantities of edible oils produced in Tunis are frequently admixed with the best brands of French and Italian edible oils, in order to mask their somewhat harsh taste.

The solid fatty acids of olive oil consist of palmitic and a minute proportion of arachidic acid. *Hehner and Mitchell* [2] did not obtain

[1] *Gazz. Chim. Ital.* 27, ii. 1.   [2] *Analyst*, 1896, 328.

stearic acid crystals from olive oil; therefore absence of stearin must be taken as proven.

Holde [1] endeavoured to resolve the mixed solid fatty acids of olive oil into their components, and obtained a small quantity of an acid of the melting point 72-72·8° C. and molecular weight 368·7. It is left open to doubt whether this acid is lignoceric acid (melting point 80·5° and molecular weight 368). This disposes of the statement previously made by *Holde and Stange* [2] that olive oil contains "oleodaturin," the "daturic" acid having been found to represent a mixture of acids (cp. Vol. I. p. 161).

Tolman and Munson [3] found the amounts of solid fatty acids (by the lead-salt ether method) in eighteen samples of Italian olive oils to vary from 5·0 per cent (in a Tuscany oil of the iodine value 80·7) to 17·72 per cent (in a Bari oil of the iodine value 81·2). Thirty-eight Californian olive oils furnished from 2·0 per cent (in a Santa Barbara oil of the iodine value 84·7) to 12·96 per cent (in a Cloverdale oil of the odine value 81·9) of solid fatty acids.

These numbers seem to be somewhat conflicting, but they dispose finally of the statement, first made by *Gerhardt*,[4] that olive oil contains, as a rule, about 28 per cent of solid glycerides.

Tunisian oils from Sfax contain, according to *Bertainchand*,[5] up to 25 per cent of solid fatty acids. Hence these oils deposit "stearine" at +9° to +10° C. The following table supplies some details :—

	Solid Fatty Acids.	Liquid Fatty Acids
	Per cent.	Per cent.
Olive oil from the North (Tunis, Bizerte, Cap-Bon, Medjerdah)	15	85
Oil from the Centre (Sousse, Mahdia, Monastir) .	21	79
Oil from Sfax	25	75
Oil from the South (Gabès, Gafsa, Djerba) . .	15	85

In order to free the Sfax oils from the excess of "stearine," it is necessary to "demargarinate" them (cp. Chap. XIII.).

The liquid glycerides were formerly considered to consist of practically pure olein (notwithstanding a conjecture of *Mulder* as to the presence of an unsaturated fatty acid other than oleic), but *Hazura and Grüssner* have shown that the liquid portion of olive oil contains also linolic acid, approximately in the proportion of 93 oleic acid to 7 linolic acid. Hence the calculated iodine value of the liquid fatty acids would be 96·56.

Milliau, Bertainchand, and Malet [5] found in Tunisian olive oils from Bizerte, Tunis, Sousse, Sfax, and Gafsa the following respective iodine values of the liquid fatty acids : 105·7 ; 113·4 ; 116·5 ; 118·2 ; and

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[1] *Berichte*, 1905, 1250.   [2] *Berichte*, 1901, 2406.
[3] *Journ. Amer. Chem. Soc.*, 1903, 956.
[4] *Chimie organique*, tome 2, p. 901.
[5] *Bull. de la Direction de l'Agric. et du Comm. Tunis*, 1903 (viii.), 167.

106·9. More recent results by *Bertainchand* : Région du Nord, 95·48-107·66 ; Région du Sahel, 98·37-109·32 ; Région de Sfax, 103·74 ; Région de Gafsa, 103·5-111·95 ; Région du Sud, 95·37-105·4.

The *minimum* iodine value of the liquid fatty acids in the above-mentioned eighteen Italian olive oils, examined by *Tolman and Munson*,[1] was 89·8 [2] (Tuscany oil of the iodine value 80·7), and the *maximum* 98·4 (in an Abruzzi oil containing 13·51 per cent of solid fatty acids). The lowest iodine value of the liquid fatty acids of the thirty-eight Californian olive oils was 88·9 (in a Napa oil of second expression), and the highest iodine value of the liquid fatty acids 99·6 (in a Chico oil containing 5·12 per cent of solid fatty acids).

By catalytic reduction of olive oil with hydrogen and colloidal palladium in the cold *Paal and Roth* [3] obtained a solid fat, softening at 43° C., completely liquid at 47° C., and having the iodine value 9. The amount of hydrogen absorbed was three times the theoretical one. Reduction with nickel as a catalyst requires a higher temperature.

Hydrogenation of olive oil has also been effected at an elevated temperature by means of osmium dioxide, obtained in the reacting mass itself from osmium tetroxide (*F. Lehmann* [4]).

Free Fatty Acids.—The best and finest edible oils should contain practically no free fatty acids. Even the salad oils are practically devoid of free fatty acids, as they contain as a rule no more than 0·2-0·5 per cent of free fatty acids. Inferior oils exhibit larger amounts. The longer the oil is allowed to remain in contact with the fleshy part of the fruit, the greater will be the production of free fatty acids (cp. Vol. I. p. 50). The exceedingly rapid decomposition olive oil undergoes when left in contact with the marc, is undoubtedly due to a ferment. Indeed, *Tolomei* [5] isolated a ferment, " olease," to the action of which he ascribes the rapid fermentation taking place in stored marc.

In order to show how the proportion of free fatty acids varies with the manner of gathering the fruit, I append the following table (due to *O. Pollatschek*) : [6]—

Fresh Fruit—	Free Fatty Acids. Per cent.
Gathered by hand, fresh	0·8
Gathered by hand after 24 hours . . .	0·85
Knocked off with the aid of poles, fresh . .	1·4
Knocked off with the aid of poles, after 24 hours	5·4

Besides this ferment, fungi, such as *Penicillium glaucum* and *Saccharomyces olei* (discovered by *van Tieghem*) contribute to the hydrolysis, they on their part most likely producing a lipolytic enzyme. It therefore follows that in order to prevent hydrolysis the oil must be separated as carefully as possible from the putrescible marc. Once hydrolysis has set in, olive oil, like other oils, becomes rancid on exposure to the

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[1] *Journ. Amer. Chem. Soc.*, 1903, 956.
[2] This number does not necessarily point to the absence of linolic acid, since the "liquid" fatty acids very likely contained some saturated fatty acids.
[3] *Berichte*, 1908, 2283 ; 1909, 1547.
[4] *Archiv d. Pharm.*, 1913, **251**, 152.   [5] *Atti R. Accad. dei Lincei*, 1896.
[6] *Chem. Revue*, 1907, 4.

atmosphere. The very high percentage of fatty acids in bagasse oils, as also in sulphur oils (see p. 346), is thus readily explained. From a very rancid olive oil *Scala* [1] isolated œnanthylic aldehyde ; formic, acetic, butyric, œnanthylic acids, and some soluble acids, presumably azelaic and suberic acids. The acetyl value of an old commercial oil was 10·6 (*Lewkowitsch*). In the following table some further data are given.

Free Fatty Acids in Olive Oil

Description of Sample.	Number of Samples.	Free Fatty Acids as Oleic Acid.	Observer.
		Per cent.	
Commercial oil	49	Less than 5	Archbutt
,, ,, ...	66	5-10	,,
,, ,, ...	44	10-15	,,
,, ,, ...	1	20-25	,,
,, ,, ...	11	3·86-11·28	Thomson and Ballantyne
,, ,, (Syrian) . .	1	23·88	,,
,, ,, (Californian) .	3	1·55-8·33	Moerck
,, ,, (European) .	3	0·97-1·09	,,
,, ,, (Italian) . .	18	0·57-2·79	Tolman and Munson
,, ,, (Californian) .	38	0·20-3·51	,,

The following table, culled from observations of *Mastbaum*,[2] shows in an instructive manner the changes which the oil undergoes in stored olives. The olives were " bagassa " olives which had to be stored, owing to the impossibility of working them up immediately.

Oil from	Free Fatty Acids.	Iodine Value.	Acetyl Value.
	Per cent.		
Fresh olives	0·33	76·3	4·8
Olives preserved five months—			
(*a*) In brine, without removing the brine .	6·72	76·6	10·1
(*b*) In running water	6 08	76·7	15·6
(*c*) In brine, the brine being removed at intervals	23·26	77·2	25·1
(*d*) By drying . . .	49·02	77·7	30·9

Olive oils containing more than 5 per cent of free fatty acids are not suitable for lubricating purposes ; they are also unsuitable for burning, as they cause charring of the wick.

The **unsaponifiable matter** in olive oil, as in all vegetable oils, is phytosterol. The *minimum* and *maximum* amounts of unsaponifiable matter recorded for a large number of samples are 0·46 and 1·42 per cent respectively.

[1] *Staz. Sperim. Agric. Ital.* 30, 613.
[2] *Chem. Revue*, 1904, 66 ; cp. also Lewkowitsch, *Jahrbuch d. Chem.*, 1904 (xiv.), 430.

In a " fine Malaga " olive oil *Archbutt* found 1·3 per cent of unsaponifiable matter melting at 41°-42° C. and having the iodine value 259. In some de-acidified pulp oil the same observer found 2·49 per cent of unsaponifiable matter having the specific gravity (at 60° F.) 0·9346, melting point 50·5°-52·5° C., iodine value 105·4 (another specimen had the iodine value 158·9), yield of mixed acetates 105·2 per cent (saponification value 85·3 and melting point 35°-38° C.).

Olive oil is the type of a non-drying oil. Hence it shows in the *Maumené* test, as also in the heat of bromination test, the smallest rise of all vegetable oils, and absorbs also the lowest amount of oxygen in *Livache's* test (Vol. I. p. 471). The lower qualities become more readily oxidised ; hence " olive oil grease " contains notable amounts of lactones as also of oxidised fatty acids. At higher temperatures even good olive oils, if spread on lead powder, become oxidised.

The influence which blowing with air at 100° C. exercises was examined by *Procter and Holmes* [1] with the following result :—

	Hours.	Specific Gravity.	Refractive Index.	Iodine Value.
Original oil . . .	...	0·912	1·4695	86·0
Blown oil . . .	3	0·913	1·4696	86·0
,, ,, . . .	6	0·913	1·4697	82·0
,, ,, . . .	9	0·913	1·4698	80·0
,, ,, . . .	12	0·913	1·4699	80·0
,, ,, . . .	15	0·914	1·4700	79·0
,, ,, . . .	18	0·914	1·4700	79 0
,, ,, . . .	21	0·915	1·4700	79 0
,, ,, . . .	24	0·918	1·4701	76·0

On account of its comparatively high price olive oil is adulterated to an enormous extent. How far the blending of various olive oils of different qualities should be considered as sophisticated must be decided in each given case. Undoubtedly " finest Nice oil," prepared by blending a genuine Nice oil with Tunisian or other olive oil, must be considered as of inferior quality. But since purely chemical tests are incapable of deciding this question, which is readily settled by the taste and by taste alone, an analyst without special experience in that direction would have to pass such oil as genuine Nice oil.

Even in judging the quality of *commercial* olive oils which are free from admixture with other oils, discrimination as to quality is important. The amount of free fatty acids alone is no longer decisive, inasmuch as, especially during latter years, owing to the failure of the harvest, low-class oils have been brought up to neutrality by eliminating the free fatty acids.[2] These oils, however, retain some impurities which cannot be removed in the de-acidifying process. Such impurities are, in addition to oxidised oil, a high amount of unsaponifiable matter. *Archbutt* [3] examined a number of such de-acidified " pulp oils " with the result set out in the following table :—

[1] *Journ. Soc. Chem. Ind.*, 1905, 1287.
[2] Cp. T. Lupieri, Italian patent 339/76/111,913, 1909.
[3] *Journ. Soc. Chem. Ind.*, 1911, 5.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Specific gravity at 60° F .	0·9167	0·9165	0·9175	0·9186	0·9169	0·9175	0·9169	0·9161	0·9179
Saponification value .	186·1	186·9	189·3	186·9	186·0	185·5	185·9	185·4	185·8
Iodine value . . .	86·4	85·1	85·8	84·4	85·5	85·6	85·0	86·5	86·2
Free (oleic) acid, per cent .	2·9	3·3	1·0	1·1	0·9	2·3	1·8	0·4	1·6
Unsaponifiable matter, per cent .	2·49	2·34	2·08	2·70	3·30	3·32	3·23	2·98	2·67
Efflux time¹ of 50 c c from Redwood's Viscometer at 60° F (seconds) .	516	450	437	478	480	561	524	428	465

¹ Normal olive oil, 430-446 seconds.

The amount of oxidised acids was not determined.

Furthermore, the qualities of the oils are lowered by admixing with them either such de-acidified oils or even sulphur olive oils.

A method for the detection of sulphur olive oil in expressed olive oil has been based by *Halphen* [1] on the conversion of sulphur compounds into thiosulphates, which remain in solution when the soap is salted out by sodium sulphate. Fifty c.c. of the sample are saponified with 12 c.c. of a solution of 100 grams of pure sodium hydroxide in 75 c.c. of water, by heating to 110° C. in a porcelain basin. The heating is then continued until the mass ceases to froth, the temperature reaching then about 160° C. The mass is continually stirred until the temperature has fallen to 110° C. The finely granulated soap is dissolved in 200 c.c. of hot water, and the solution agitated until cold. The solution is then shaken with 100 c.c. of a saturated solution of sodium sulphate, after which 20 c.c. of a 33 per cent solution of copper sulphate are introduced, and the liquid thoroughly stirred and filtered. The object of adding the copper sulphate is to convert into soluble copper salts foreign substances occurring in certain expressed olive oils, which give a brown precipitate with silver nitrate. If the filtrate is not faintly green, it should be treated with an additional 0·2 c.c. of the copper sulphate solution and again filtered. To 100 c.c. of the clear filtrate there are then added 5 c.c. of a solution consisting of 1 part of a 5 per cent solution of silver nitrate, with 5 parts by volume of glacial acetic acid, and the whole is gently heated to the boiling point, then cooled, and rendered slightly alkaline with ammonia. In the presence of sulphur olive oil a brown or black precipitate is obtained.

E. Milliau [2] recommends saponifying the oil with concentrated potash, adding a little sodium bicarbonate and decomposing with hydrochloric acid. The gas evolved from oils containing 0·05 per cent of carbon bisulphide blackens lead acetate paper. However, oils which have been heated previously for one hour at 130° C. no longer blacken lead acetate paper. In such cases *Milliau* distils 50 grms. of the oil with 10 c.c. of amylalcohol, collects 5 c.c. of the distillate, and mixes this with a quarter of its volume of neutralised kapok oil and a few cgms. of powdered sulphur in a sealed tube in boiling water, when oils containing only 0·1 per cent of carbon bisulphide are stated to give a deep red colouration. (The method rests on the principle that the reducing substances of kapok oil or cotton seed oil, which give rise to the *Halphen* reaction, are not removed by distillation.)

In the following lines adulteration with other oils than lower quality olive oils will be considered. Oils that are usually employed for this purpose are sesamé, rape, cotton seed, soya bean, poppy seed, arachis, and even lard oils. Olive oils sold under fancy names are, as a rule, adulterated.

The tables of characteristics contain a very exhaustive list of numbers, so that by carefully scrutinising them, methods for the

[1] *Journ. Pharm. Chim.*, 1905 (xxi.), 54.

[2] *Compt. rend.*, 1911 (153), 1021 ; cp. also M. Cusson, *Ann. des falsif.*, 1909 (2), 409 ; F. Marre, *Rev. gén. chim. pure et appl.*, 1912, 174.

examination of a given sample, suspected of being adulterated, can
be derived. It is therefore only necessary to emphasise the most
salient points.

The **specific gravity** of olive oil ranges from 0·916 to 0·918 at
15° C., but may rise to 0·920 in the case of commercial oils expressed
at a higher temperature. Oils of high specific gravity usually exhibit
a dark colour. The influence of free fatty acids on the specific gravity
may be gathered from the table given Vol. I. p. 313, which must,
however, not be taken as representing typical results. If the specific
gravity of a pale olive oil is above 0·918, it must be looked upon with
suspicion, *i.e.* as possibly adulterated with *sesamé, cotton seed*, or *poppy
seed oils*. Adulteration with *rape* or *arachis oil* is not indicated reliably
by the specific gravity.

The **melting and solidifying points of the fatty acids** (titer
test) also furnish useful indications as to the purity of an olive oil. It
would, however, be hazardous to draw too far-reaching results from
this test. Hence the tabulated observations recorded in the second
edition of this work have been omitted here.

The **iodine test** constitutes the most valuable means of detecting
adulteration. Olive oil has nearly the lowest iodine absorption of any
oil that might be used for adulteration. As a rule, the iodine value
of an olive oil should lie between 81·6 to 84·5. There occur, however,
undoubtedly genuine oils, the iodine values of which exceed these
numbers. Thus the oil from the Colombaio olive reaches 86, oil from
some Portuguese varieties (sevilhana, mançanilha, cordovil) 87 (*Klein*),
Californian oils 88, and in the case of a Dalmatian oil as high a figure
as 92·8 was obtained (this has been even exceeded by an olive oil from
the Punjab, of the iodine value 93·67 [1]). Still, these cases are notable
exceptions, and an oil with an iodine value exceeding 85 must, as a rule,
be looked upon with suspicion. With regard to Tunisian and Algerian
oils, the table given on p. 363 shows that genuine oils, having what
may be termed the normal iodine value of olive oil, occur side by side
with oils characterised by exceptionally high iodine values. It would,
however, not be permissible to generalise as *Marcille* [2] has done, who
from a systematic examination of genuine olive oils produced in Tunis,
concludes that the iodine value from 90 to 92 may be taken as character-
istic of this class of oil.

Paparelli [3] studied the causes of the variability of the iodine values,
and arrived at the following conclusions :—The more mature the olives
the higher is the iodine absorption of the oil. Old and rancid oil has,
as a rule, a slightly lower number than fresh oil. The method of pre-
paring the oil has also its influence. Oil from the pulp absorbs slightly
less iodine than that obtained by grinding pulp and " pits " together ;
oils extracted by solvents show lower values than expressed oils ; again,
oils from pits are characterised by higher numbers than oils from the

[1] Thomson and Dunlop, *Analyst*, 1906, 282. A Mogador oil absorbing 94·3 per cent
of iodine may actually have been a specimen of " Argan Oil " (see p. 322).
[2] *Ann. chim. anal. appl.*, 1907, 12, 188.
[3] *Journ. Soc. Chem. Ind.*, 1892, 848.

fresh fruit. Tho greatest variation, however, is due to the variety of the olive tree from which the fruit is obtained.

In the absence of abnormal oils, a high iodine absorption may indicate adulteration with as little as 5 per cent of a *drying oil* (poppy seed, hemp seed, soya bean oil) or 15 per cent of *sesamé, cotton seed*, and *rape oils*. Less positive results are obtained in the presence of *arachis oil*, as the lowest values recorded for that oil almost coincide with the highest value observed for olive oil.

It may be pointed out that the iodine values of the semi-solid and of the liquid portions into which olive oil separates on partial solidification almost coincide (*Goldberg* [1]).

The **saponification value** only leads to definite results (in the absence of mineral oils) if large quantities of *rape oil* are present.

In the **elaïdin test** olive oil yields of all oils the hardest elaïdin, and requires the shortest time for solidification. The elaïdin reaction can however only be used as a preliminary test. The effect of an addition of rape or cotton seed oil to olive oil is shown in the following table compiled from observations published by *Archbutt* : [2]—

Kind of Oil.			Minutes required for Solidification, at 25° C	Consistence.
Olive oil			230	Hard, but penetrable
Olive oil + 10 per cent of rape oil		.	320	Buttery
,, + 20 ,, ,,			From 9 to 11½ hours	Buttery
,, + 10 ,, cotton seed oil			From 9 to 11½ hours	Very soft
,, + 20 ,, ,,			More than 11½ hours	butter

Regarding the proposal to measure the effect of a foreign oil on the hardness of the elaïdin quantitatively by using *Legler's* method (Chap. V. p. 362), it should be borne in mind that olive oil, after exposure to sunlight for a fortnight, no longer yields a solid elaïdin (*Gintl*). *Farnsteiner* [3] has shown that the amount of oleic acid converted into elaïdic acid depends greatly on the conditions under which nitrous acid acts on the oil. Indeed, the amount of unchanged liquid acid varies so much in different experiments that no quantitative method can be based on the conversion of oleic acid into elaïdic at present.

In the **thermal reactions** olive oil gives lower values than any other vegetable oil. *Lengfeld and Paparelli* assert that there exists a proportionality between the iodine number and the **Maumené** test of olive oil, the oil of the highest iodine value giving the greatest rise of temperature. Their results, arranged by the author according to the magnitude of the iodine values, do not, however, bear out fully the correctness of this rule.

[1] *Journ. Soc. Chem. Ind.*, 1897, 447.   [2] *Ibid.*, 1886, 308.
[3] *Zeits. f. Unters. d. Nahrg· u. Genussm.*, 1899, 8.

Olive Oil. No.	Iodine Value. Per cent.	Maumené Test. °C.
1	77·28	35
2	78·42	33 5
3	78·51	33 5
4	78·52	34
5	79·50	36
6	79 53	34 5
7	80 80	37
8	81·45	38
9	81·50	35
10	81·70	34
11	83·35	37 5
12	85·44	36 5
13	87·15	41

Tortelli [1] claims for the results obtainable with his thermoleometer (see Vol. I. p. 484) such great accuracy as to render the determination of the iodine value superfluous. In the author's opinion this conclusion is tantamount to begging the question.[2] Moreover, *Tortelli* overlooks adulteration with animal oils.

The proportionality between iodine number and **heat of bromination test** is shown in the following table (*Archbutt*) : [3]—

Olive Oil.	Iodine Value. Per cent.	Heat of Bromination. °C
Malaga	78 4	14 2
.	78 7	13 55
...	78 9	13 8
Malaga	79 3	13 8
.	81 4	14 2
	81 4	14 35
Gallipoli	82 0	14 4
,,	82 1	14 5
,,	82 5	14·5
...	84 2	14 45

An examination of the **unsaponifiable matter** in an olive oil [4] free from fraudulent admixtures with mineral oils [5] is required if admixture of lard oil be suspected, the presence of which would be unmistakably detected by the phytosteryl acetate test. The alcohol in the unsaponifi-

[1] *Bolletino chimico farmaceutico*, 1904, 193.
[2] Lewkowitsch, *Jahrbuch d. Chem.*, 1904 (XIV.), 438.
[3] *Journ. Soc. Chem. Ind.*, 1897, 311.
[4] It should be noted that in Germany olive oil is "denatured" with rosemary oil, which of course increases the amount of unsaponifiable matter.
[5] Although adulteration with mineral oil had almost disappeared, no doubt owing to its easy detection, cases of adulteration with mineral oil were recorded in 1910 and 1911. A. Cutolo, *Bolletino della Società di Naturalisti in Napoli*, anno XXIII., vol. xxiii., 1910. Curiously enough Cutolo recommends a colour reaction for the detection of mineral oil in olive oil.

able matter from olive oil melts at 135·5°-136·5° C. (*Bömer*), 135°-135·5°
C. (*Gill and Tufts*).   Its acetate melts at 120·3°-120·7° C. (*Gill and Tufts*).

Green olive oils should be tested for copper, which may have been
added intentionally in the form of a salt, or may have been absorbed
from the soil or leaves treated with " Bordeaux mixture."   Copper is
best detected in the manner described above (Vol. I. Chap. IV.).

In the following lines I collate the most useful tests for the detection
of those oils which occur as adulterants [1] in commercial olive oils :—

1. **Arachis Oil.**—Iodine absorption ; as a rule, the amount of
iodine absorbed will be higher than that of normal olive oil.   *Determina-
tion of arachidic acid* (see " Arachis Oil," p. 310).

Tortelli's statement that an arachis oil free from arachidic acid can
be prepared by demargarinating is not borne out by the author's
experiments.   Several samples of demargarinated arachis oil examined
in the author's laboratory still contained considerable proportions of
arachidic acid, sufficient to render easy the detection of an admixture of
such arachis oil to olive oil.

In order to ascertain definitely whether genuine Tunisian olive oils
did contain such considerable amounts of arachidic acid—viz. 0·34- ,
0·87 per cent—as some commercial " guaranteed pure " Tunisian oils
gave, an examination was made by *Archbutt* [2] of undoubtedly genuine
Tunisian and of Algerian oils procured by the author and *Bontoux*,
with the result set out in the following table :—

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[1] It may be pointed out that adulterated olive oils, especially olive oils for technical
purposes, have again appeared in the market in considerable quantities.   In Italy it
has been found necessary for the protection of the olive oil industry to promulgate a law
(in 1908) aiming at the repression of frauds in the olive trade.

[2] *Journ. Soc. Chem. Ind.*, 1907, 453 ; 1185.

Tunisian and Algerian Oils from	Colour.	Specific Gravity at 60° F.	Free Acid (as Oleic Acid).	Saponification Value.	Iodine Value (Wijs).	Unsaponifiable Matter.
			Per cent.	Per cent. 191·9	Per cent. 85·4	Per cent. 0·95.
1. Sousse, Tunis, 1906-1907 harvest. "Congealing."	...	0·9170	...			
2. Sousse, Tunis, 1906-1907 harvest	Yellow	0·9175	...	191·6	86·2	0·81
3. Bône-Guelma, Algeria, 1906-1907 harvest.	Golden yellow	0·9167	...	191·7	83·2	0·83
4. Medjez-Amar, Algeria, Province of Constantine, 1906-1907 harvest. "Non-congealing."	Golden yellow	0·9173	...	190·3	90·5	0·97
5. Tunis. Variété Chétni, Mornag	Pale yellow (primrose)	0·9178	...	190·4	94·7	0·92
6. Tunis. Variété Chemlali, Sfax.	Yellow	0·9162	...	190·6	80·2	0·88
7. Tunis. Variété Chemlali, Gabès	Pale yellow (primrose)	0·9169	...	190·9	86·9	0·77
8. Tunis. Variété Chétui, Bizerte.	Yellow	0·9171	...	189·2	91·1	0·91
9. Tunis. Variété Besbassi, Rhadès-Tunis	Brownish yellow	0·9164	...	190·4	82·7	1·15
Algerian Oils from						
1. Guelma, expressed from mixed olives.	Pale grass green	0·9173	1·1	189·9	89·7	0·89
2. Guelma, expressed from the olives "Verdale" and "Roussette."	Pale greenish yellow	0·9969	4·5	189·6	90·4	0·81
3. Medjez-Amar from the olives "Roussette" and "Blanquette." 1st expression	Golden yellow	0·9169	0·9	189·6	89·0	0·88
4. 2nd expression	Brownish yellow	0·9171	0·9	189·2	89·8	0·96
5. Gnelbat bou Sba from "Roussette" olives. 1905 crop	Primrose yellow	0·9173	0·4	190·1	90·1	0·80
6. 1906 crop	Pale primrose yellow	0·9178	0·5	189·2	90·3	0·72
7. Duvivier from the olives "Blanquette" and "Roussette."	Yellowish green	0·9178	2·3	189·0	88·5	0·78
8. Tlemcen	Golden yellow	0·9166	0·5	189·6	84·9	0·92
9. Mizrana, near Tizi Ouzou. From mixed olives, but especially 'Chemlali' and "Abetkou", varieties.	Pale greenish yellow	0·9168	0·6	191·3	83·7	0·74
10. l'Oued Aissi, near Tizi Ouzon. From mixed olives.	Primrose yellow	0·9164	1·6	190·7	82·4	0·77
11. Mirabeau, near Tizi Ouzon. From mixed olives from the valley of l'Oued Bougdoura	Pale greenish yellow	0·9165	2·1	191·0	82·5	0·98
12. Makonda of the ordinary mixed olive oil of Mizrana.	Pale greenish yellow	0·9165	2·4	191·3	82·4	0·88

In Renard's arachidic acid test the following results were obtained : —Tunisian Oils, Nos. 1 and 2, gave some crystals at 15° C. No. 3 gave only a trace, and No. 4 none. After filtering and washing, the first crystals from No. 1 left 0·0123 grm. of acids of melting point 55·6° C. On recrystallising from 10 c.c. of 90 per cent alcohol, nothing separated after standing one hour at 15° C. In a second experiment with oil No. 1 only 0·0007 grm. remained after washing the crystals which had separated at 15° C.

10 grms. of oil No. 2 gave 0·001 grm. fatty acid at 15° C. after washing. From 10 grms. of the oils Nos. 5, 6, 7, 8, 9 no " arachidic acid " was obtained. On the first crystallisation of the solid acids, from 90 per cent alcohol at 15° C., small quantities of crystals were obtained from oils Nos. 5, 8, and 9, and a considerable quantity from Nos. 6 and 7. After filtering and washing with 90 per cent alcohol the following amounts remained :—

No. 5	.	.	.	·0014 grm.
No. 6	.			·0105 grm. of melting point 56·7° C.
No. 7			.	·0018 grm.
No. 8	.			·0102 grm. of melting point 55·6° C.
No. 9	.	.	.	·0025 grm.

On recrystallising the acids Nos. 6 and 8 from 5 c.c. of 90 per cent alcohol nothing separated even after standing for more than an hour at 4° C.

The last twelve samples yielded no trace of arachidic or lignoceric acid. In contradistinction to the Tunisian oils, none of the solid fatty acids from Algerian oils yielded even traces of a crystalline precipitate from a solution of 90 per cent alcohol at 15° C.

Adulteration even of commercial olive oils with arachis oil is at present on the increase. In the case of residuum oils, *Archbutt*[1] obtained positive indications with *Bellier's* qualitative test, without, however, being able to isolate arachidic acid. The presence of this flocculent precipitate he ascribes to the large amounts of unsaponifiable matter which these oils contain.

2. **Sesamé Oil.**—Specific gravity ; iodine absorption of the oil and of its liquid fatty acids ; and *Baudouin's* test (see " Sesamé Oil," p. 220). In order to avoid errors caused by abnormal oils, such as Tunisian, etc., the liquid fatty acids should be examined. The oils enumerated in table on p. 363 were examined in the author's laboratory with *Villavecchia and Fabris's* furfural solution (cp. p. 220). No. 6 gave no colouration whatever, whereas No. 8 gave a very distinct colour test. No. 5 of the Algerian oils gave a distinct colour test, whereas No. 11 gave no colouration.[2] The other oils gave very faint colourations only.

3. **Cotton Seed Oil.**—Specific gravity ; melting point of fatty acids, iodine absorption of the oil, iodine value of the liquid fatty acids. Colour reactions as confirmatory tests (p. 203).

[1] *Journ. Soc. Chem. Ind.*, 1911, 6.
[2] Cp. R. Marcille, *Ann. des falsif.*, 1909, 224 ; Zega and Todorovic, *Chem. Zeit.*, 1909, 103.

It should be borne in mind that some genuine olive oils give the *Becchi* reaction very distinctly (*Tortelli and Ruggeri*): in doubtful cases, the liquid fatty acids should therefore be tested. It should further be remembered that heated cotton seed oil fails to give the *Halphen and Becchi* tests.

As an illustration of how far it is possible to detect adulteration by examining the liquid fatty acids, I have calculated the following table, in which the iodine values of the liquid fatty acids of the mixtures named are worked out for the lowest and highest values of olive and cotton seed oils respectively.

Olive Oil.	Cotton seed Oil.	Iodine Value of Liquid Fatty Acids.			
Per cent.	Per cent.	I.	II.	III.	IV.
100	0	95	95	104	104
95	5	97·6	97·8	106·15	106·35
90	10	100·2	100·6	108·3	108·7
85	15	102·8	103·4	110·45	111·05
80	20	105 4	106·2	112·6	113·4
0	100	147	151	147	151

It will be seen that by this test alone, small quantities of cotton seed oil cannot be detected ; still more difficult is its detection if arachis oil be present.

4. Rape Oil.—Iodine absorption of the oil and of the liquid fatty acids ; melting and solidifying points of the mixed fatty acids ; *saponification value* and *iodine value of the " solid " fatty acids* (see p. 257). With regard to arachidic acid cp. p. 256. A method for the detection of rape oil by fractional precipitation of the fatty acids with lead acetate is given by *Kreis*,[1] who claims to be able to show the presence of as little as 5 per cent of rape oil thereby.

5. Castor Oil. — Specific gravity ; *acetyl value* ; (cp. also 10) behaviour with solvents.

6. Curcas Oil (used in Portugal, according to *Hiepe*, as an adulterant of olive oil).—Iodine absorption. Admixtures of even 10 per cent are said to be detected by the intense reddish-brown colouration the sample assumes a short time after treatment with nitric acid and metallic copper (in the elaïdin test).

7. Lard Oil.—Melting point of fatty acids ; viscosity ; odour of lard on warming. *Phytosteryl acetate test.*

8. Drying Oils.—Iodine value. Thermal tests. Bromide test.

9. Fish Oils.—The detection of fish oil in olive oil is required in the case of olive oil intended for preserving sardines, etc. (Since the body oil of the sardine becomes intermixed with the olive oil used for preserving the fish, fish oils are contained to some extent in olive oil

[1] *Chem. Zeit.*, 1913, 877.

drawn from the tins containing preserved fish.[1]) Fish oils are detected by the taste and smell, especially on warming, and notably by the high iodine value of the sample. In doubtful cases the isolation of insoluble brominated fatty acids must be resorted to. If required the oil must be tested for the presence of metals dissolved from the tins.[2]

H. Bull and L. Saether [3] attempt to determine approximately the quantity as also the nature of the oil used in the preservation of sprats. The principle of their method is based on the determination of the insoluble bromides both in the body oil of the preserved sprats and in the outer oil contained in the tins. It must be noted that several assumptions are made which most seriously interfere with the correctness of the conclusions drawn from the results. The body oil is best prepared by washing the sprats with a little ether to remove the adhering outer oil, drying slightly, crushing the sardines in a mortar, and expressing in a press. This method is preferable to extraction with ether which furnishes an emulsion.

10. **Grape Seed Oil**, stated by *Tortelli* to be used for the adulteration of olive oil, would be detected by a notable acetyl value of the sample ; cp. also " 5. Castor Oil."

11. **Maize Oil**, also stated by *Tortelli* to be used for adulterating olive oil, can be detected by the high iodine value of the sample and of its liquid fatty acids. The pronounced " grainy " taste of maize oil would preclude its use as an adulterant of the edible qualities and restrict its employment to the adulteration of commercial oils.

12. **Hydrocarbons.** — Determination of unsaponifiable matter. Adulterants falling under this class are : colourless vaseline and mineral oils.

When testing a suspected olive oil, it should be borne in mind that the adulterator has kept pace with the progress of analytical methods, and that, in order to render detection more difficult, he no longer uses one single oil, but prefers a mixture of several oils. Thus olive oil is frequently adulterated with 8 to 10 per cent of a mixture consisting of equal parts of poppy seed, cotton seed, sesamé, and arachis oils (*Jean* [4]). In a case of this kind the determination of the iodine value of the liquid fatty acids will furnish the first and most important indication, after the presence of sesamé oil has been ascertained by means of the *Baudouin* test.

The uses of olive oil have been incidentally mentioned in the foregoing pages. It need, therefore, only be briefly pointed out that the better qualities of olive oil are used in enormous quantities as an edible

[1] Thus an olive oil of the iodine value 78·9, employed for preserving sardines, and taken from the tins after two months, one year, and two years, absorbed 99·02, 109·05, and 126·2 per cent of iodine respectively.—Klein, *Zeits. f. angew. Chem.*, 1900, 559. Similarly, an oil of the iodine value 84·9 used in the preservation of sprats and taken from the tins after one year, showed the iodine value 97·2.—Henseval and Deny, *Trav. de la Station Maritime à Ostende*, 1903.

[2] Cp. G. Salomone, *Giorn. Farm. Chim.*, 55, 241.

[3] *Chem. Zeit.*, 1910, 732.

[4] *Annal. de chim. anal.*, 1898, 218.

oil—the edible oil *par excellence*. Very large quantities of good edible
oils are exported, chiefly from Bari, for the preservation of sardines,
sprats, etc. Lower qualities are used in the arts as burning oils, lubri-
cating oils (for this purpose de-acidified pulp oils came into the market,
cp. above, p. 356), wool oils, and soap oils. High class medicinal soaps
are made chiefly from the best commercial olive oils. Textile soaps of
the best quality, such as soaps for degumming silk and for washing
best woollen cloth, are made from bright commercial oils. Soaps for
these purposes are either " hard " or " soft." Calico printers require,
for the best class of goods, soaps made exclusively from olive oil. For
textile soaps (as also for household soaps in the South of Europe) the
highly acid bagassa oils, " olive oil grease," and sulphur olivo oils
are used.

" Olive oil grease " which, as stated above, contains considerable
amounts of lactones, as also of oxidised acids, is thereby enabled to
retain, after saponification with caustic soda, a larger amount of water
than pure olive oil, and is therefore used by itself for the manufacture
of soap containing less than 63 per cent of fatty acids. It is also used
extensively in Marseilles in the manufacture of mottled soap (*Savon
marbré de Marseilles*), and generally in the South of Europe in admixture
with arachis and sesamé oil in larger or smaller quantities, according
to colour and quality, for the manufacture of household soap.

The " sulphur olive oils " do not contain such large amounts of
oxidised acids as do the pulp oils, and very small amounts of lactones
only. The " sulphur oils " are easily saponified on account of their high
proportion of fatty acids, and yield a hard, green (due to the presence
of chlorophyll) soap, which is used to a considerable extent in the
textile industry in this country, and is mostly sold as a soap contain-
ing 60 per cent or at most 62 per cent of fatty acids. As its green
colour helps to differentiate it easily from other textile soaps, the
colouration of textile soaps from other " stock " with green colouring
matters has gained some vogue. In Southern Europe the sulphur
oils are very largely used in the manufacture of household soaps.

The use of olive oil in the industry of artificial leather is extending.[1]

The introduction of sulphonated oils (Vol. III. Chap. XV.) has greatly
reduced the consumption of the tournant olivo oil (see above, p. 346).

OLIVE KERNEL OIL

French—*Huile de noyaux d'olive*.   German—*Olivenkernol*.
Italian—*Olio di noccioli d' oliva*.

For table of characteristics see p. 369.

Olive kernel oil is the oil obtained (by pressure or extraction) from
the seeds contained in the olive stones. What had been formerly

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[1] Cp. J. Wallner, *Chem. Zeit.*, 1910, 23.

described as olive kernel oil was a highly rancid olive oil containing such quantities of olive kernel oil as would be expressed from the seeds on grinding the mare and crushed kernels with water (p. 345 [1]) in the second and third expressions.

Olive kernel oil obtained by expression in the cold has a golden yellow colour ; the oil expressed in the hot possesses a greenish tint, whereas kernel oil extracted with solvents is dark green, no doubt owing to the presence of chlorophyll.

The taste of the expressed oil is sweetish, somewhat resembling that of almond oil, without, however, possessing the characteristic bland taste of olive oil.

The kernels constitute about 2·5 per cent of the weight of the entire fruit ; they yield from 25 to 28 per cent of oil.

Olive kernel oil contains about 10 per cent of solid fatty acids, amongst which were identified stearic and palmitic acids, but not arachidic acid.   The chief constituent of the liquid fatty acids is oleic acid ; small quantities of linolic acid also occur in the oil.

The freshly expressed oil is practically free from fatty acids.   If the expressed mass is allowed to dry and then extracted with solvents, an oil containing a high proportion of free fatty acids is obtained, owing to hydrolysis having occurred during the prolonged contact of the oil with the organic matter.

The solubility of the oil in alcohol does not materially differ (in contradistinction to former statements) from that of olive oil.

In other respects also the oil closely resembles olive oil.   Olive kernel oil naturally occurs in those olive oils which have been obtained from olive marc crushed together with the kernels.

Klein proved by special experiments that the belief prevalent amongst olive growers, that crushing of the kernels together with the marc causes olive oil to turn rancid easily, is groundless.   *Mingioli* [2] arrived at conclusions diametrically opposed to those of *Klein*, but *Marcille* [3] has confirmed *Klein's* conclusions.   *Marcille* proved by experiments that the kernels contain an enzyme which acts on their non-fatty constituents (starch, sugar, glucosides), whilst exhibiting an extremely feeble lipolytic action.   Hence the very short time during which, in practice, the broken kernels remain in contact with the olive pulp can have no deteriorating influence on the quality of the olive oil.

The press residue from olive kernels should yield a good feeding cake ;   indeed, where the kernels are kept separate from the broken shells, the cakes obtained on pressing are used for feeding purposes. The broken shells are used as fuel.   Proposals have been made frequently to work up these residues for the production of acids, methylalcohol, acetone, etc., by subjecting them (together with the exhausted olive marc residues) to a process of dry distillation (cp. p. 347).

[1] Klein, *Journ. Soc. Chem. Ind.*, 1898, 1055.

[2] *Bolletino della Società degli Agricoltori italiani*, 1906.

[3] *Bulletin de la Direction de l'Agriculture du Commerce et de la Colonisation, Tunis*, 1907.   Cp. French patents 399,341 and 399,342, *Las Industrias del Olivo*.

Physical and Chemical Characteristics of Olive Kernel Oil

Oil obtained by	Specific Gravity.	Saponification Value.	Iodine Value.	Refractive Index.	Observer.
	At 15° C.	Mgrms. KOH.	Per cent.	At 25° C.	
Expression of fresh kernels	0·9184-0·9191	182·3-183·8	86·99-87·8	1·4682-1 4688	Klein
Drying and subsequent extraction of the pressed kernel . . .	0·9193	181·2	87·1	1.4673	,,

CALOPHYLLUM OIL

French—*Huile de Calophyllum.* German—*Kalophyllumol.*
Italian—*Olio di Calophyllum.*

For table of characteristics see p. 370.

Calophyllum oil is obtained from the nuts of *Calophyllum ino-phyllum*, L. (=*Balsamaria inophyllum*, L.), a tree[1] indigenous to tropical Asia and the coast of East Africa. The nuts described by *Hooper* are Indian nuts, and the oil is known in India as " Laurel Nut Oil," " Domba Oil," and " Alexandrian Laurel Oil."[2] The oil is also known under the names " Poonseed Oil," " Tacamahac Fat " (Réunion, Nossi-bé), from *C. Tacamahaca*, " Njamplung Oil," " Calaba Oil " (Martinique and Guadeloupe), from *C. Calaba.* Another local name for the oil is " Pinnay Oil."

In the examination of a large consignment of nuts of *Calophyllum inophyllum* the author[3] found them to consist of 62·9 per cent of shells and mesocarp and 37·1 per cent of kernels. The latter yielded by expression in the hot (in a hydraulic press) 35·6 per cent of oil.

The specimen of oil examined by *Fendler*[4] was obtained from *Calophyllum* nuts exported from the island Yap (Jap, Carolines). The kernels yielded from 50·5 to 55 per cent of an oil containing about 15 per cent of a green resin, removable by treatment with a solution of sodium carbonate. The characteristics obtained for the oil, containing 15 per cent of the resin (having the neutralisation value 198), are given in the table (p. 370). This crude oil had the acid value 28·45, and yielded 0·25 per cent of unsaponifiable matter. In the *Livache* test the oil absorbed after 18 hours 0·25 per cent oxygen, and after 136 hours 1·84 per cent.

The characteristics of the oil, freed from resin, are also given in the table (p. 370).

The oil consists of the glycerides of palmitic, stearic, and oleic acids.

The natives use the oil for medicinal and illuminating purposes. Recently efforts have been made to introduce this oil under the name of " Ndilo-oil " (Udilo Oil, Dilo Oil) as a specific against rheumatism. Owing to the poisonous properties of the oil, and especially of the resin contained in the crude oil, it cannot be used as an edible oil.

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[1] The wood is frequently sold as Indian Mahogany.
[2] Cp. 4th edition of this work Vol. II., table facing p. 192.
[3] Unpublished observations.   [4] *Apotheker Zeit.*, 1905, No. 1.

Physical and Chemical Characteristics of Calophyllum Oil

	Specific Gravity	Solidifying Point	Melting Point	Saponification Value	Iodine Value	Refractive Index at 15° C.		
	At ° C.	° C.	° C.	Mgrms. KOH.	Per cent.	Butyro-refract. At 40° C.	Observer.	Observer.
Oil containing resin	16	0·9315[1]	1·5	7·5	196·4	95·3	1·4772	Hooper
	15	0·9415	3	8	198·7	92·8	76	Grimme
	25	0·9428		separates "stearine" on standing,	196·0			Fendler
Oil freed from resin					191·0	86·0		,,

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Fatty Acids + Unsaponifiable	Solidifying Point	Melting Point	Neutralisation Value	Mean Molecular Weight	Iodine Value	Refractive Index at 45° C.	Observer.
	Per cent.	° C.	° C.	Mgrms. KOH.		Per cent.		
Fatty acids freed from resin	78·3[2]	32·5	36·5	192·3	289	94·8	1·4654	Grimme *
		33	38	194	289·2	92·2		Fendler
				Liquid Fatty Acids	Liquid Fatty Acids	Liquid Fatty Acids		
				190·7	294·2	114·5		,,

[1] Pharm. Journ. Trans., 1889 (10), 525 ; cp. also Journ. Soc. Chem. Ind., 1901, 642.

[2] In addition thereto the oil gave 18·3 per cent of a saponifiable resin (Grimme, Chem. Revue, 1910, 265).

·COFFEE BERRY OIL

French—*Huile de café.*   German—*Kaffeebohnenol.*
Italian—*Olio di caffe.*

For tables of characteristics see p. 372.

Coffee berry oil—obtained by extracting coffee berries with solvents (*Caffea arabica*, L.)—has an intense greenish-brown colour and a faint odour of raw coffee.   On roasting the berries the oil is very little changed.   *Hilger and Juckenack*,[1] state that the loss of oil on roasting the berries amounts to 9 to 10 per cent; berries glazed with sugar lose about 20 per cent.   Java berries yielded on extraction with petroleum ether 9 per cent of oil (*Warnier* [2]).

According to *H. Meyer and A. Eckert*, stearic acid does not occur in coffee berry oil; the mixed fatty acids are stated to consist of 50 per cent of linolic, 2 per cent of oleic, 25-28 per cent of palmitic, 0·5 per cent of capric, $1\text{-}1\frac{1}{2}$ per cent of daturic acid, and 10 per cent of carnaubic acid.[3]   In the author's opinion the carnaubic acid found by *H. Meyer and A. Eckert*[4] must have been derived from coffee berry wax (see "Vegetable Waxes" below), which was extracted together with the oil, for that specimen of coffee berry oil yielded no less than 21·2 per cent of unsaponifiable matter.

[1] *Analyst*, 1897, 287.
[2] *Pharm. Weekblad*, 1907 (44), 1080
[3] *Monatsh. f Chem.*, 1910 (31), 1227.
[4] Cp. *Jahrbuch d. Chem.*, 1910 (xv.), 124.

Physical and Chemical Characteristics of Coffee Berry Oil

Specific Gravity. At ° C.	Solidifying Point. ° C.	Melting Point. ° C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Maumené Test. ° C.	Observer.
15 0·9510-0·9525	5·3 / 6·3		165·1-173·37	85·89-87·34 (78·65)		De Negri and Fabris[1]
24·5 0·942	5·6	8·9	176·2-177·3 / 177·5	85·3-86·8 / 85 / 90·1-91·2	53-55	Spaeth[2] / Warnier[3]

Physical and Chemical Characteristics of Coffee Berry Oil—continued

Refractive Index		Observer.
At 25° C.	1·4777-1·4778[4]	Spaeth
Butyro-refractometer "Degrees." At 25° C.	79-79·25 / 81·5	Spaeth / Warnier

[1] *Annali del Lab. chim. delle Gabelle*, 1893, 253. [2] *Chem. Zeit.*, Rep., 1895, 292.
[3] From Java beans. [4] *Meyer und Eckert*. The oil yielded 21·2 per cent of unsaponifiable substances.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point. °C.	Melting Point. °C.	Neutralisation Value Mgrms. KOH.	Iodine Value. Per cent.
36 – 34	38-40	172-178	88·82-90·35
...	...	...	(81·8)

BEN OIL

French—*Huile de ben.*   German—*Behenöl.*   Italian—*Olio di ben.*

For tables of characteristics see p. 374.

Ben oil occurs in the seeds of the ben nut from *Moringa pterygosperma,* syn. *oleifera,* and *Moringa aptera,* Gärt.[1] The Moringa trees are indigenous to India, Arabia, and Syria, and were introduced into Jamaica from the East Indies in the year 1784.[1] *Moringa pterygosperma* has also been found in Northern Nigeria, and in Dahomey. The root has a horse-radish like taste and is eaten in India by the Europeans in place of horse-radish. Hence the tree is known as " Horse-radish tree."

The Jamaica seeds consist of 40 per cent of husks and 60 per cent of kernels. Genuine ben oil from Jamaica gave, on filtering at 17° C., 60 per cent of liquid material, and 40 per cent of a nearly white solid fat. A specimen of the latter obtained by the author [2] from the *Imperial Institute* represents at the ordinary temperature a whitish or yellowish-white translucent mass melting at about 25° C. Other specimens described in the table of characteristics are liquid at the ordinary temperature, and some " stearine " separates from them on standing at about 0° C.

Northern Nigerian seeds submitted to the author by the Imperial Institute contained 33·27 per cent of oil. The seeds consisted of 8 per cent of husks (forming a light-coloured skin), and 92 per cent of kernels, so that the shelled kernels would yield 36·16 per cent of ben oil ; on the average 552 seeds weigh 100 grams.

These seeds were expressed in two stages on a semi-large scale, and yielded a cold pressed oil and a hot pressed oil.[3] The examination of these two oils in the author's laboratory gave the following numbers :—

	Cold-pressed crude Ben Oil.	Hot-pressed crude Ben Oil.
Specific gravity at 40° C. water at 40°=1	0·9018	0·8984
Acid value	19·71	100·5
Saponification value . .	179·2	178·7
Unsaponifiable matter .	1 67 per cent	2·69 per cent
Iodine value . . .	100 3	88
Titer test of the fatty acids .	32° C.	38·2° C.

[1] *Bull. Imp. Inst.,* 1904, 117.
[2] Lewkowitsch, *Analyst,* 1903, 343.
[3] With regard to the composition of the cakes see *Bull. Imp. Inst.,* 1908, 361.

Refined ben oil has a slightly yellowish colour, is odourless, and has a sweet taste.

Ben oil is stated to consist of the glycerides of oleic, palmitic, and stearic acids, and of a solid acid of high melting point; according to Völcker,[1] this acid is identical with behenic acid, melting point 76° C. [arachidic acid ?]. The phytosterol isolated from ben oil by L. van Itallie[2] and C. H. Nieuwland melted at 131-135° C.

In the East ben oil serves as a cosmetic; it used to be employed in the "maceration" process for extracting perfumes from flowers.

Physical and Chemical Characteristics of Ben Oil

Specific Gravity.		Solidify-ing Point.	Saponification Value.	Iodine Value.	Butyro-refractometer.		Observer.
At ° C.		° C.	Mgrms. KOH.	Per cent.	° C.	"De-grees."	
15·5	0·91998 [3]	8·8 [5]	185·6 [4]	111·8 [3]	40	60·5 [3]	Lewkowitsch
,,	0·91840 [4]		186·17·	109·9 [4]	,,	59·0 [4]	,,
,,	0·91267 [5]		187·7 [5]	72·2 [5]	,,	50 0 [5]	,,
,,			184·6 [3]	112·6 [6]	,,	59·0 [3]	,,

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point	
° C. Titer Test.	Observer.
37·2-37·8	Lewkowitsch

On the strength of experiments made in Kingston, Jamaica, in 1817, ben oil was considered an exceedingly valuable oil for delicate machinery, and was credited with the property of not readily turning rancid. From the above-given notes (supported by experiments made in the author's laboratory with refined oil) this assumption must be looked upon as erroneous. Ben oil becomes rancid just like any other oil, having the same consistence and composition, the state of rancidity of a given specimen depending on the manner in which it has been kept. The oil if properly refined would yield a good edible oil, and should be a valuable lubricating oil for delicate machinery if kept properly.

[1] Liebig's *Annal.*, 1847 (64), 342.   [2] *Arch. d. Pharm.*, 1906 (244), 159.
[3] Freed from "Stearine."   [4] Portion solid at 0°.
[5] Oil from *Moringa pterygosperma*.   [6] Commercial oil.

STROPHANTHUS SEED OIL [1]

French—*Huile de strophante.*   German—*Strophantusöl.*
Italian—*Olio di strofanto.*

Physical and Chemical Characteristics of Strophanthus Seed Oil

Specific Gravity.		Solidifying Point.	Melting Point.	Saponifica- tion Value.	Iodine Value.	Observer.
At ° C.		° C.	° C.	· Mgrms. KOH.	Per cent.	
13	0·9254			187·9	73·02	Mjöen [1]
15	0·9249	− 6	+2	194·6	101·6	Bjalobrzewski [2]

This oil is obtained from the seeds of *Strophanthus hispidus*, which contain 22 per cent of oil.[3] The oil has a brownish-green colour, appearing yellowish-brown by transmitted light.

The sample examined by *Bjalobrzewski*, containing 12 per cent of free fatty acids, yielded traces of a volatile oil. Amongst the volatile acids formic acid was identified ; from the insoluble fatty acids oleic, stearic, and arachidic acids were isolated (by fractional distillation of the ethylic esters).

The melting point of the insoluble fatty acids was 28°-30° C.

SENEGA ROOT OIL

French— *Huile de Polygala de Virginie.*   German—*Senegawurzelol.*
Italian—*Olio di Senega.*

The oil contained in the roots of *Polygala Senega*,[4] L., to the extent of 4·55 per cent, is readily soluble in the usual solvents ; it dissolves with difficulty in xylene, and is only partially soluble in petroleum ether.

The specimen examined by *Schroeder* contained 12·8 per cent of unsaponifiable matter ; this consisted chiefly of resinous substances, insoluble in petroleum spirit. The volatile fatty acids are stated to contain valeric acid, and also salicylic acid. The acid value of the oil was 37·9, and its acetyl value 34·46.

The unsaturated fatty acids had the iodine value 82·4. The saturated fatty acids melted at 61° C. *after* repeated recrystallisation ; their mean

[1] Mjöen, *Arch. d. Pharm.,* 1894 (234), 283. For a description of the several Strophantic species found in East Africa cp. K. Braun, *Der Pflanzer,* 1910, 291.

[2] *Journ. Soc. Chem. Ind.,* 1901, 817.

[3] According to " Riedel's " commercial reports, 1913, 33, extraction with petroleum ether yields from 31·4 to 32·3 per cent of oil.

[4] A. Schroeder, *Arch. d. Pharm.,* 1906 (244), 638, and *Journ. Soc. Chem. Ind.,* 1906, 128.

molecular weight was 260. The composition of the Senega root oil is given by *Schroeder* as follows :—unsaponifiable matter, 12·78 per cent ; palmitin, 7·9 per cent ; olein, 79·3 per cent. The high Reichert-Wollny value is in conflict with the saponification value.

Physical and Chemical Characteristics of Senega Root Oil

Specific Gravity.		Saponification Value.	Iodine Value.	Reichert-Woolny Value.	Insoluble Acids + Unsaponifiable.
At ° C.		Mgrms. KOH.	Per. cent.	c.c. $\frac{1}{10}$ norm. KOH.	Per cent.
18	0·9616	193·8	81·8 [1]	6·43 (?)	85·8
			78·4 [2]		

<center>LYCOPODIUM OIL</center>

Rathje [3] obtained, by extracting lycopodium spores with chloroform, 49·2 per cent of a bright yellowish-green oil, having the following characteristics :—

Oil—

Specific gravity .	0·93617
Saponification value .	195·0
Iodine value .	81·0
Reichert-Meissl value .	7·3
True acetyl value .	44·1
Refractive index .	1·4671
Unsaponifiable matter .	0·43 per cent

Fatty Acids—

Fatty acids +unsaponifiable matter .	88·0 per cent
Melting point .	39°-40° C.
Neutralisation value .	202·0
Mean molecular weight .	278·0
Iodine value .	91·8
Iodine value of the liquid fatty acids .	98·7

The extracted oil had the acid value 18·6. According to *Rathje*, the oil contains " lycopodic acid," 81 per cent ; dihydroxystearic ("lycopodium acid"), 3·2 per cent ; small quantities of stearic and palmitic (about 1 per cent of each), and about 2 per cent of myristic acid. [It should be pointed out that the proportions of solid acids were determined by *Partheil and Ferié's* (faulty) lithium salt method.] The nature of the volatile acids, which must be present in notable quantities, was not investigated.

[1] Oil containing the unsaponifiable matter.
[2] Oil free from the unsaponifiable matter.
[3] *Arch. d. Pharm.*, 1908, 699.

STERCULIA OIL—OIL OF JAVA OLIVES [1]

French—*Huile de Sterculia*; *huile de l'olive de Java*. German—
· *Sterculiaöl* (*Java Olivenöl*). Italian—*Olio di Sterculia*; *olio
d' oliva di Java*.

For tables of characteristics see p. 379.

This oil is obtained from the seeds of *Sterculia fœtida*, L., a tree
widely distributed in the Dutch Indies, Indo-China, the East Indies,
and the Malayan Archipelago. It is cultivated in these countries,
as also in Guayana (Cayenne) on account of its wood (which in its green
state has an unpleasant smell, and is therefore termed in the trade
" bois puant " (stinking wood). The seeds are known in commerce
as " Olives of Java," " Kaloempang beans," " Beligno seeds," or
" Sterculia kernels."

The average weight of a seed is 2·4 grms. They are covered with
an outer parchment-like easily removable skin of violet or blackish
colour. Below the skin is found a dark fleshy mass—pulp—which
adheres to the husk of the pleasantly tasting kernel.

Wedemeyer [2] obtained from the skin and pulp by extraction (the
nature of the solvent is not stated) 9·8 per cent of a yellow buttery fat,
and from the kernels 46·6 per cent of a liquid, light yellow oil. The
whole seeds yielded 30·3 per cent of a liquid, light yellow oil. *Greshoff* [3]
found 58·65 per cent of oil in the dry seeds (which originally contained
7·8 per cent of water). The characteristics placed in the tables against
Wedemeyer refer to an oil obtained from the whole seeds by expression.
This expressed oil is of a pale yellowish colour. *Wedemeyer's* specimen
contained 2·6 per cent of free fatty acids, and 1·7 per cent of unsaponifi-
able matter. The acetyl value of the mixed fatty acids (determined
by *Benedikt and Ulzer's* faulty method) was 23·5.

Bontoux [4] examined separately the oils obtained from the pulp and
kernels of seeds furnishing 17 per cent of skin and pulp, 30 per cent of
husks, and 53 per cent of kernels. The skin and pulp yielded by
extraction with carbon bisulphide 28·6 per cent and the kernels 53·6
per cent of oil respectively. The fatty matter obtained from the former
was a light yellow pasty mass, becoming clear on warming above 30° C,
The expressed fat has a pleasant odour and taste.

Hooper [5] ascertained the following characteristics of a Java almond
oil from kernels yielding 34 per cent of oil :—

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[1] Since the name "Java Olives" appears misleading, I prefer to name this oil
"Sterculia Oil."
[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1906 (xii.), p. 210.
[3] *Chem. Zeit.*, 1906, 856.
[4] Lewkowitsch, *Technologie et analyse chimiques des huiles, graisses et cires*,
traduit par E. Bontoux, vol. ii. p. 902.
[5] *Annual Report, Indian Museum*, 1907-1908, p. 13.

Oil—

Specific gravity at 30·5° C.	.	.	.	0·919
Saponification value	.		.	.	199·3
Iodine value	.	.	.	.	83·0

Fatty Acids—

Insoluble acids + unsaponifiable	.	.	95·6 per cent
Titer test .	.	.	.	.	.	31·5° C.

The extracted *kernel oil* is liquid, but slightly viscous ; the expressed oil has a somewhat insipid taste and odour, recalling that of earth.   Oil obtained by expression or by extraction with petroleum ether is yellow, whereas oil extracted with carbon bisulphide exhibits a fine cherry-red colour.   This colouration must be due to the action of traces of sulphur in the solvent, for in the *Halphen* test both the expressed oil and that extracted with petroleum ether give a very intense cherry-red colour.

The oil obtained by extraction or by expression from the *whole seed* is liquid and slightly viscous.   It has the same colour, taste, and odour as the *kernel oil* (of which it contains more than 85 per cent), but on standing " stearine " separates at the ordinary temperature.   The characteristics of the pulp oil and of the *kernel oil* are given separately in the tables.

The most characteristic property of the kernel oil, which is shared by the whole oil but not by the pulp oil (*Bontoux*), is its behaviour (first observed by *Wedemeyer*) on heating to 240°-245° C., when it is suddenly converted, with spontaneous generation of heat, into an india-rubber-like, solid substance.   If a somewhat large quantity (about 1000 grms.) of the oil be heated, the spontaneous generation of heat, if not prevented by cooling, causes the oil to ignite and become carbonised throughout its whole mass.   If the oil be heated for a short time to 240° C. and the temperature be not allowed to rise above 250° C., a tough india-rubber-like substance is obtained, which remains elastic on exposure to the air, and is insoluble in the usual solvents.   No doubt this property is due to a process of polymerisation similar to that of castor oil.   It cannot, however, be caused exclusively, as in the case of castor oil, by hydroxy-lated fatty acids, as the acetyl value of the fatty acids from the kernel oil, determined by *Lewkowitsch's* method, was only 18·8 (*Bontoux*). The extraordinary rise of temperature in the *Maumené* test (see table of characteristics) would seem to offer some clue as to the characteristic behaviour of the oil on heating ; very likely some unknown fatty acids are contained in sterculia oil, an indication of which is also given by variation of the saponification and iodine numbers (see tables of characteristics), and by the exceptionally low neutralisation value of the insoluble fatty acids (cp. Vol. III. " Polymerised Sterculia Oil ").

In a *Soleil-Ventzke* polarimeter (in a 200 mm. tube) very slight rotation was observed.   The viscosity in *Engler's* viscosimeter was 6·52 at 20° C.

In Java the oil is used by the natives for culinary purposes, and as a burning oil.

Physical and Chemical Characteristics of Sterculia Oil

	Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Maumené Test.	Refractive Index.	Observer.
	At ° C.	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm KOH	° C.	At 40 ° C.	
Pulp oil . .	...	172·1	81·4 [1]	...	...	...	Bontoux
		192·8 [2]	58·7 [2]				"
		193·8 [3]	56·5 [3]				"
		173·4 [2]	81·4 [2]				"
Kernel oil . .	...	174·3 [3]	83·1 [3]				"
Whole oil . .	0·9260 (15)	187·9	76·6	0·8	158	1·4654	Wedemeyer [4]

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Fatty Acids + Unsaponifiable	Solidifying Point.	Melting Point.	Neutralisation Value	Saponification Value.	Iodine Value.	Observer.
	Per cent.	° C	° C	Mgrms. KOH	Mgrms. KOH.	Per cent.	
Pulp oil . .	95·7	43 (Titer)	46·5	199·2	203·8	57·7	Bontoux [3]
Kernel oil . .	95·4	viscous thickening at 25·27°		185·6 [5]–195·7 [6]	190·8 [5]–186·8 [6]		
Whole oil . .	95·6		...				Wedemeyer

[1] Expressed oil.   [2] Extracted by petroleum ether.   [3] Extracted by carbon bisulphide.

[4] Expressed oil from the whole seeds.

[5] Means of five determinations with fatty acids of different preparations, dried at 110-115° C.

[6] Means of five determinations with fatty acids of different preparations, dried at 40° C. in vacuo.

The seeds from *Sterculia appendiculata*, K. Schum., a tree growing to a height of 200 to 300 ft. in Usambara (East Africa), consists of 45 per cent of shell and 55 per cent of kernel. The latter yields 28·76 per cent of oil ; the whole seed gives 15·82 per cent. The oil is pale yellow and on standing some " stearine " separates.

C. Grimme [1] ascertained the following characteristics :—

Oil—

Solidifying point	– 2° C.
Saponification value	185·0
Iodine value	82·4
Refractive index at 20° C. . . .	1·4729
Unsaponifiable matter	6·39 per cent

Fatty Acids—

Insoluble fatty acids + unsaponifiable matter .	91·12
Melting point	34°-35°
Neutralisation value	175·2 [2]
Mean molecular weight	320·6 [2]
Iodine value . .	86·7
Refractive index at 40° C. . . .	1·4630

TROPÆOLUM OIL [3]

French—*Huile de cresson d'Inde.* German—*Tropaeolumöl. Kapuzinerkressenol.* Italian—*Olio di tropeolo.*

The oil obtained from the seeds of *Tropæolum majus*, L., is a buttery mass, melting at a slightly elevated temperature. On standing, a very considerable portion crystallises from the oil ; the crystals consist of pure trierucin.

The iodine value of tropæolum oil is 73·75 ; since this value differs but slightly from the theoretical number of trierucin—72·2—the oil may be considered as consisting chiefly of trierucin.

PARADISE NUT OIL [4]

French—*Huile de noix de paradis.* German—*Paradieskörneröl.* Italian—*Olio di noci del paradiso.*

For table of characteristics see p. 381.

The kernels of *Lecythis Zabucajo*, Aubl., *L. ollaria*, L. (*Quatelé Zabucajo*), a large tree belonging to the *Myrtaceæ*, and indigenous to Guiana and Brazil, contain from 50 to 51 per cent of oil.

The fruit known as " sapucaia nut " grows in almost the same manner as does the Brazil nut, but the kernel is larger, its skin is slightly wrinkled, and its taste somewhat sweeter than that of the " Para "

[1] *Chem. Revue*, 1910, 180.
[2] These numbers must be accepted with reserve.
[3] Gadamer, *Arch. d. Pharm.*, 1899, 273, 472.
[4] De Negri, *Journ. Soc. Chem. Ind.*, 1898, 1156.

(Brazil) nut. The tree is found nearly all over Brazil, and the kernels are greatly estimated as an article of food. Hence such small consignments as arrive in the markets of Manaos or Belem are usually sold privately and very little is exported. The sapucaia nuts arriving occasionally in this country are also sold under the name of "Brazil nuts."

The characteristics given in the table were determined by *De Negri*, with an oil obtained from Sapucaia nuts by extraction with petroleum ether. The oil was slightly yellow, odourless, and had an insipid taste ; its acid value was 3·19. It was insoluble in cold glacial acetic acid, but dissolved in an equal volume of the hot acid. *De Negri* found the acetyl value of 44·08, this number must, however, be accepted with reserve.

Physical and Chemical Characteristics of Paradise Nut Oil

Specific Gravity.	Solidify- ing Point.	Saponification Value.	Iodine Value.	Refractive Index. Butyro-refracto- meter.	Observer.
At 15° C.	°C.	Mgrms. KOH.	Per cent.	At 15° C.	
0 895 (?)	4	173 6	71 64	61·3-61·5	De Negri

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.	Observer.
°C.	°C.	Per cent.	
28·5	37·6	72 3	De Negri

SECALE OIL

French—*Huile de scigle ergoté.* German—*Mutterkornol.*
Italian—*Olio di segala cornuta.*

Secale oil is obtained from *Secale cornutum*, which yields by extraction 30 per cent of a brownish-yellow oil having the following characteristics :—

[TABLE

	Mjöen.[1]	Fabris and Settimj.[2]	Rathje.[3]
Oil—			
Specific gravity . . .	0·9254 at 13° C.	0·927 at 15° C.	0·9250 at 15° C.
Solidifying point . .	..	− 10° C.	..
Saponification value . .	178·4	191 4	178·4-180·2
Iodine value . . .	71·1	74 6	73·4-74·5
Reichert-Meissl value . .	0 20	..	0 61-0·67
True acetyl value . . .	.	..	27·44
Butyro-refractometer " degrees " at 25° C. . .	.	65	.
Refractive index . .	.	..	1·4685
Maumené test. . .	.	51° C.	..
Unsaponifiable . .	..	..	0 36 per cent
Fatty Acids—			
Insoluble acids + unsaponifiable	96·3	98 5 per cent (?)	95·8-96 6
Solidifying point . .	..	30°-31° C.	..
Melting point . . .	39 5 -42° C.	37°-38° C.	38°-39° C.
Neutralisation value . .	.	..	183
Iodine value . . .	.	75·8	77·2
Iodine value of the liquid fatty acids	..	104	82·2

The insoluble fatty acids consist, according to *Fabris and Settimj*, of 64 per cent of liquid and 46 per cent of solid acids. This agrees much better with the melting point of the mixed fatty acids than does *Rathje's* statement that the oil contains 5 per cent of palmitic, 68 per cent of oleic, and 22 per cent of " hydroxyoleic " acids.

CANARI OIL [4]

French—*Huile de Canari.*   German—*Canariol.*
Italian—*Olio di Canari.*

For table of characteristics see p. 384.

" Java almond oil " is obtained from the seeds of *Canarium commune*, L. (*Bursera paniculata*, Lam., = *Colophonia mauritiana*, D. C.), a tree indigenous to the Moluccas and Malabar ; it is cultivated in tropical Asia, where the seeds serve as a foodstuff in place of sweet almonds (which they resemble in shape and taste). One thousand air-dried seeds weigh 5934·3 grms., yielding 809·8 grms. (13·64 per cent) kernels. One thousand kernels weigh 520 grms.

The seeds yield on extraction with solvents 65·7-68·6 per cent of oil ; the extracted meal contains 34·7 per cent of proteids. On pressing the seeds, 56·1 per cent of oil was obtained.[5] The oil extracted from the kernels has a pale-yellow colour and a pleasant, mild taste. At 15° C. " stearine " commences to separate. The unsaponifiable matter in the oil amounts to 0·44 per cent. The acid value of the specimen examined by *Wedemeyer* was 22·8, its acetyl value is stated as 8·4 ; that of samples examined by *Pastrovich* was 1·3 for extracted oil, and 0·84 for

[1] *Arch. d. Pharm.*, 1894 (234), 278.
[2] *Atti del VI. Congresso Internaz. di chimica applicata, Roma*, 1907, vol. v. 761.
[3] *Arch. d. Pharm.*, 1908, 697.
[4] Wedemeyer, *Seifensieder Zeit.*, 1907, 26.
[5] Pastrovich, *Chem. Zeit.*, 1907, 782.

expressed oil. The acetyl value determined on the mixed fatty acids
was 16·39 for the extracted, and 15·68 for the expressed oil. These
acetyl values must, however, be accepted with reserve.

On separating the insoluble fatty acids by means of the lead-salt-
ether method, *Pastrovich* obtained 44·6 per cent of solid fatty acids
melting at 54·45° C., and having the mean molecular weight 266. On
precipitating fractionally the magnesium salts of the solid acids, stearic
and palmitic acids were identified. On oxidising the liquid fatty acids
(55·4 per cent), considerable quantities of dihydroxystearic acid and
small quantities of sativic acid were obtained. No hexabromides were
found, hence linolenic acid appears to be absent. The fatty acids of this
oil consist, therefore, approximately, of 44·6 per cent of palmitic and
stearic acids,[1] 43 per cent of oleic acid, and 12·5 per cent of linolic acid.

The seeds from *Canarium oleosum* (Lam.) Engl. (= *Canarium micro-
carpum*, Willd.), a *Burseracea*, are flat-shaped, 2-3 cm. long, 1-1·5 cm.
broad, and consist of 15·14 per cent of husk and 84·86 of kernels. The
latter yield 68·63 per cent of a pale-yellow oil, furnishing the following
characteristics : [2]—

Oil—

Solidifying point .	12·5° C.
Saponification value	197·0
Iodine value	63 0
Refractive index at 20°	1·4664
Unsaponifiable matter	0 97 per cent

Fatty Acids—

Insoluble fatty acids + unsaponifiable matter .	94·76 per cent
Melting point	44·46° C.
Neutralisation value	195·2
Mean molecular weight	287·7
Iodine value	63·7

The husks contain 34·53 per cent of oil having the following char-
acteristics :—

Solidifying point .	16 5° C.
Saponification value	183·5
Iodine value	78·2
Refractive index at 20° C.	1·4584
Unsaponifiable matter	4·88 per cent
Fatty acids	89·93 per cent

The seeds from *Canarium polyphyllum*, a tree widely distributed in
New Guinea, yielded on extraction with ether 68·23 per cent of an oil
having the following characteristics : [3]—

Solidifying point .	19°-20° C.
Melting point	30° C.
Saponification value	200·2
Iodine value	59·74
Reichert-Meissl value	4·41 [4]
Refractive index at 21° .	1·4750

[1] Oudemans, *Journ. f. prakt. Chem.*, 1860 (81), 356 ; 1866 (99), 409, states that
myristic acid occurs in this oil.

[2] C. Grimme, *Chem. Revue*, 1910, 178.

[3] M. Krause, *Der Tropenpflanzer*, 1913 (7), 147.

[4] This value is much too high to agree with the saponification value 200·2.

Physical and Chemical Characteristics of Canari Oil

Specific Gravity.	Melting Point.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Maumené Test.	Refractive Index. Butyro-refractometer at 40° C.	Observer.
°C. (water at 40=1)	°C.	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	°C.	"Degrees."	
0·8953	18-28·5	193·5	64·7	0·1	59	49·5	Wedemeyer
0·9050		194·3	65·6	0·0		51·2	Pastrovich

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Fatty Acids +Unsaponifiable.	Specific Gravity.	Solidifying Point in Capillary Tube (Titer Test).	Melting Point of the Insoluble Fatty Acids (in Capillary Tube).	Neutralisation Value.	Saponification Value.	Mean Molecular Weight from Neutral Value.	Iodine Value.	Refractive Index. Butyro-refractometer at 40° C.	Observer.
Per cent.	°C. (50 water at 50=1)	°C.	°C.				Per cent.		
95·5	0·8825	37·2	40·4	191·1					Wedemeyer
95·5		41·0		201·6	205·1	278·6	67·2 Liquid Fatty Acids 110·4	35·7	Pastrovich

Castor Oil Group

In this group I comprise grape seed oil and castor oil. These two oils (pending further confirmation as regards grape seed oil) are remarkable for their high proportion of hydroxylated fatty acids, as indicated by their high acetyl values. Owing to this composition castor oil is miscible with alcohol. This property is not shared by grape seed oil ; for this reason it is open to doubt whether grape seed oil is related to castor oil, a doubt which is further supported by the circumstance that the grape seed oils described by the several observers differ greatly (see below) in their characteristics.

GRAPE SEED OIL

French—*Huile de pépins de raisin.* German—*Traubenkernöl.*
Italian—*Olio di vinacciuoli.*

For tables of characteristics see p. 388.

Grape seed oil is obtained from grape seeds (from *Vitis vinifera*, L.) by expression or by extraction. The freshly expressed grape yields 25 per cent of seeds containing 6 to 20 per cent of oil, which is prepared by grinding the dried seeds (by exposure to the air) to a coarse meal, intermixing with about 25 per cent of water, and expressing first in the cold and then in the hot. The quantity of oil in the seeds depends on the kind of grapes and the climate in which they are grown. According to some writers the seeds from white grapes are richer in oil than those from black, and sweet grapes yield more oil than those containing little sugar. Other writers state that the black grapes grown in warm countries are richer in oil (containing 10 to 20 per cent), and that such oil is of superior quality. Whereas the average of grape seed oil recovered in some French mills was 8 to 10 per cent, in Wurtemberg 10 to 11 per cent of crude oil are generally obtained. The seeds contain the largest amount of oil at the time of vintage ; on storing the seeds the quantity of oil decreases considerably.

The oil obtained by cold expression has a golden-yellow colour, and is free from odour. Oil from stored seeds is darker and has a slightly bitter flavour. Oil of the second expression is brown and has a bitter taste. Grape seed oil extracted by means of solvents is dark ; but is said to become perfectly colourless by filtering over animal char. The numbers recorded in the table refer to extracted oil. The oil dissolves easily in glacial acetic acid at 70° C. ; the solution becomes turbid at 66·5° C. In 96 per cent alcohol it dissolves only partially.

The specimens of oil examined by various observers differ considerably. The iodine values of the two oils examined on the one hand by *Horn*, and on the other by *De Negri and Fabris*, agree tolerably well, and would point to similar oils. Grape seed oil does not dry on exposure to air, or only after a long time (*De Negri and Fabris*). Very

different from these oils are the grape seed oils examined by *Ulzer and Zumpfe* and by *Fabris and Settimj* [1] (see below).

According to *Horn*, the most prominent characteristic of grape seed oil is, its high *acetyl value*, placing it, in this respect, in close relationship to castor oil. Since this number was obtained by *Benedikt and Ulzer's* method, it stands in need of confirmation. The high specific gravity stated by *Horn*, in conjunction with the low saponification value, would seem to confirm the high proportion of hydroxy acids. Yet, the specific gravity ascertained by *De Negri and Fabris*, and the immiscibility with alcohol, negatives a high proportion of hydroxy acids. The low saponification number found by *De Negri and Fabris* (practically identical with that stated by *Horn*) speaks, however, in favour of *Fitz's* statement,[2] that grape seed oil contains considerable quantities of erucic acid. This was isolated from the ether-soluble lead salts as a solid acid of the melting point 33° C., yielding, on fusion with caustic potash, a considerable amount of arachidic acid. The sample examined by *Horn* had the acid value 16·2.

The very high iodine value recorded by *Ulzer and Zumpfe* [3] would place the oil amongst the drying oils. An examination by the lead-salt-ether method, and the subsequent examination of the liquid fatty acids by *Hazura's* method, showed that that specimen of oil contained 7 to 8 per cent of solid fatty acids (calculated on the total fatty acids),[4] most likely of stearic and palmitic acids (mean molecular weight 271, melting point 56° C., iodine value 0·4). Arachidic and lignoceric acids could not be detected. Nor could erucic acid be obtained; hence its presence is extremely doubtful. On oxidising the liquid fatty acids with potassium permanganate in alkaline solution in the cold, *Ulzer and Zumpfe* obtained: dihydroxystearic acid, considerable quantities of sativic acid, probably also linusic acid, and presumably a tri-hydroxystearic acid. Final proof, however, has not been adduced to show that the supposed tri-hydroxystearic acid, of the melting point 139° C. and molecular weight 333·9, did not consist of a mixture of other acids. The acetyl value of 43·7 found by *Ulzer and Zumpfe* cannot be accepted as confirming the presence of hydroxylated fatty acids in this grape seed oil, the acetyl value having been determined by a faulty method. It should, however, be pointed out that the specimen examined by them was readily soluble in petroleum ether. The same stricture would apply to the acetyl value given by *Fabris and Settimj*.

The conflicting statements as to its composition rendered the re-examination of grape seed oil desirable.

Such an examination has been carried out by *Fachini and Dorta*; their results are reproduced in the following table :—

[1] *Atti del VI. Congresso, etc.*, Roma, 1907, vol. v. 762.   [2] *Berichte*, 1871, 442.
[3] *Österr. chem. Zeit.*, 1905, 121.
[4] Fabris and Settimj obtained 15 per cent of solid fatty acids.

Oil from	Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Acetyl Value.	Maumené Test.	Refractive Index.	Acid Value.	Fatty Acids.
									Per cent.
Seeds from Puglie grapes, hot pressed	0·9262	189·7-189·9	129·4-129·8 (Hubl) 130·4 (Wijs)	0·4	24·7-25·0	81·5	at 15° 1·4769	7·0	92·6
Same, pressed cold in the laboratory and examined immediately	0·9260	195·5	130·4 130·7 (Wijs)		24·2-24·5		at 17° 1·4772	3·3	
Seeds from white and black grapes, seeds removed before distillation		192·3-194·9	140·1-140·7 (Wijs) 137·2 (Hubl)	0·35	23·2-23·6		at 17·5° 1·4759	4·3	
Seeds after having passed through the still		193·4	140·4 (Wijs)		23·0-24·1		at 17·5° 1·4760	4·2	
Seeds from white and black grapes pressed in the cold in the laboratory and examined immediately	0·9258	192·9	139·4 (Wijs) 136·5 (Hubl)					3·9	93·7

Physical and Chemical Characteristics of Grape Seed Oil *

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Acetyl Value.		Refractive Index.		
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. N/10 norm. KOH.	Observer.	°C.	Observer.		Observer.	At °C.		Observer.
0·926	Jobst	−11	Jobst	178·4	Horn	94	Horn					144·5[1]	Horn	25	1·4713	Ulzer and Zumpfe
0·9202	Hollandt	−15	Hollandt	178·5-	De Negri and Fabris	95·8-	De Negri and Fabris	0·46	Horn	52-54	De Negri and Fabris	43·7	Ulzer and Zumpfe			,,
0·9561	Horn	to		179		96·2		1·9	F. and S.					50	1·4623	
0·935	De Negri and Fabris	−17														
		−10	De Negri and Fabris	190	U. and Z.	142·8	U. and Z.			81-83	U. and Z.		Zumpfe		Butyro-refractometer. "Degrees."	
0·9215	U. and Z.	to														
0·925	F. and S.	−13		178·3	F. and S.	130·3	F. and S.	0·35	Fachini and Dorta	64·5	F. and S.	30·9	F. and S.	25	68·5	U. and Z.
0·9258	Fachini and Dorta	−13	F. and S.	189·7	Fachini and Dorta	136·5	Fachini and Dorta	to		81·5	Fachini and Dorta	23·25	Fachini and Dorta		70·3	F. and S.
to				to		to		0·4						50	54·5	U. and Z.
0·9262				195·5		140·4										
0·9502	Paris			179·8	Paris	96	Paris					144·5	Paris			

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
92·13 (?)	Horn	20-18	De Negri and Fabris	23·25	De Negri and Fabris	187·4	Horn	98·65	Horn
97·6 (?)	F. and S.	20	F. and S.	25·26	F. and S.			98·9-	De Negri and Fabris
92·6 (?)	Fachini and Dorta							99·05	F. and S.
								132·5	
								Liquid Fatty Acids.	
								151·7	F. and S.

1 This value requires confirmation, having been determined by Benedikt and Ulzer's method.

2 Annali del Lab. chim. delle Gabelle, 1893, 225.

The iodine value of the liquid fatty acids was 157·7. Unfortunately the foregoing examination does not settle the difficulties, inasmuch as *G. Paris*[1] found in a more recent examination of Italian grape seed oil the iodine value 96, and the acetyl value 143·1. Paris identified amongst the fatty acids erucic, linolic, oleic, stearic, and palmitic acids. He also isolated 0·57 per cent of a phytosterol, melting at 132°-130° C., having $[a]_v^{15} = -32·8°$ and yielding an acetate melting at 120°-121° C.

The oil of first expression is used locally—in France, in Wurtemberg, and in Italy—as an edible oil. The hot-pressed oil (after refining with concentrated sulphuric acid) is used as a burning oil, and would find an outlet for soapmaking if it were produced in sufficiently large quantities.[2] It has also been stated that grape seed oil is used in Italy for adulterating rape seed oil, and even olive oil.

On the strength of the exceedingly high acetyl value which *Horn*[3] found, he proposed the employment of this oil as a substitute for castor oil in the manufacture of Turkey-red oil, but the oil has been found unsuitable as a Turkey-red oil substitute.

The press cakes obtained in the preparation of the oil are used for feeding sheep and cattle, but *C. S. Fuchs*[4] has shown that the cake only contains 11·5 per cent of proteins of which only about half was digested after seventy-two hours treatment with Pepsin hydrochlorate. At the beginning of last century the cakes are stated to have been used by the poorer classes in Italy for the preparation of a tea-like beverage.

CASTOR OIL

French—*Huile de ricin*.　German—*Ricinusöl*.
Italian—*Olio di ricino*.

For tables of characteristics see pp. 400-402.

Castor oil is obtained from the seeds of *Ricinus communis*, L.

The origin of the name castor oil is due to the Spaniards and Portuguese in Jamaica having confounded the *Ricinus* plant with a totally different one, viz. *Vitex agnus castus* (Agno-Casto), abbreviated to "agnocasto." The English traders corrupted this name into "castor" in the eighteenth century (cp. De Candolle's *Origin of Cultivated Plants*).

The plant[5] seems to have been indigenous to Africa, but was transplanted to India at a very early stage of history. In fact, some writers consider it to be indigenous to India itself. The plant is found in enormous quantities in all tropical and subtropical countries, and even growing wild to-day in South America, notably in Paraguay and Argentina.

[1] *Staz. sperim. agrar. Ital.*, 1911 (44), 669.
[2] Cp. also F. Marre, *Rev. chim. pure et appl.*, 1911, 14, 186.
[3] *Mitt. des k. k. technolog. Gewerbe-Museums*, 1891, 185.
[4] *Chem. Zeit.*, 1911, 30.
[5] For the cultivation, production, preparation, and utilisation of the castor seed cp. *Bull. Imp. Inst.*, 1911, 17.

There is, therefore, an abundance of castor seeds to be obtained whenever the demand of the market increases.

In India a number of varieties are cultivated. In Bengal alone three distinct varieties of the plant are known. The first variety, growing to a height of about twelve feet, yields small, bright, black seeds, dotted all over with grey. The second variety, requiring more care in cultivation, grows to a height of about six feet, and yields somewhat larger wheat-coloured seeds. The third variety, grown along with Indian corn, furnishes the largest slightly flattened seeds of a red colour and mottled. The best quality of East Indian castor seed is known in Bombay as " painty seed."

In French Indo-China the following three species are mainly discriminated among a large variety of the *Ricinus* :—(1) the common *Ricinus* plant, *Ricinus communis*, known to the Annamites as Cây dú dú tia ; (2) the green ricinus (*ricin vert*), *Ricinus viridis*, having the same local name ; (3) the red ricinus (*ricin rouge*), *Ricinus sanguineus* (indigenous name, Cây dú dú dô).

The " St. Eustatius " castor seeds appear to be obtained from *R. Zanzibarinus* or *R. Zanzibariensis*.[1]

The most important sources of castor seed are East India, Java,[2] the Mediterranean countries, Mexico, and the United States of America. At present castor seeds are also collected commercially in Southern Nigeria and in Erythrea, and endeavours are made to create a castor seed cultivation in Formosa. By far the largest producer is East India. The exports of castor beans from India have grown considerably during the last fourteen years, whilst the Indian production of oil has decreased, owing to the expansion which the manufacture of castor oil has experienced in France, the United Kingdom, and the United States. This is illustrated by the following tables :—

Exports of Castor Seeds and Oils from East India, 1890–1904

Year ending March 31,	Castor Seeds.	Castor Oil.
	Bushels of 50 lbs.	Gallons.
1890	2,003,973	3,198,785
1891	1,925,889	3,789,628
1892	1,872,472	3,929,758
1893	2,216,556	3,095,564
1894	2,481,369	2,754,261
1895	2,631,765	3,215,887
1896	2,348,201	2,420,358
1897	2,235,778	2,397,653
1898	2,372,516	2,344,797
1899	2,710,709	2,569,725
1900	1,978,731	1,833,842
1901	1,962,121	1,843,207
1902	2,965,527	2,424,270
1903	3,509,781	2,488,910
1904	3,509,717	2,300,015

[1] Blomendal, *Pharm. Weekblad*, 1905, 42, 701.
[2] *Journ. Soc. Chem. Ind.*, 1895, 321.

Exports of Castor Seeds from India, 1904-1912

	1904-5.	1905-6.	1906-7	1907-8	1908-9.	1909-10.	1910-11.	1911-12.
	Cwts.	Cwts.	Cwts.	Cwts.	Cwts.	Cwts.	Cwts.	Cwts.
United Kingdom	452,353	479,348	649,874	1,121,035	806,789	1,026,783	1,120,251	1,109,255
France . .	266,845	286,848	277,002	267,383	333,950	250,473	272,242	382,418
Belgium . .	275,179	185,568	198,785	289,733	207,093	258,160	292,683	288,305
Italy . . .	252,010	197,240	166,268	237,028	176,223	229,394	250,991	291,470
Germany . .	193,402	136,757	203,691	70,409	109,603	82,310	150,202	73,083

Exports of Castor Oil from India, 1904-1912

	1904-5.	1905-6.	1906-7.	1907-8.	1908-9.	1909-10.	1910-11.	1911-12.
	Gallons.	Gallons.	Gallons.	Gallons.	Gallons.	Gallons.	Gallons.	Gallons.
United Kingdom .	256,975	191,034	129,102	233,583	131,308	122,984	144,056	149,004
Ceylon .	72,041	61,994	65,818	81,233	63,980	76,617	66,484	76,628
Straits Settlements . .	242,672	201,160	185,019	180,686	176,824	131,772	140,752	107,518
Hong-Kong	102,524	68,392	38,737	18,268	13,539	467	2,800	1,807
Cape Colony . .	110,814	92,070	172,802	81,495	9,063	11,877	27,732	35,525
Natal . .	212,269	255,528	231,358	215,137	73,690	74,699	93,663	98,384
Mauritius and Dependencies . .	92,582	105,867	96,602	92,415	82,414	88,736	93,489	109,233
New Zealand . . .	89,841	111,748	132,389	129,640	166,718	134,253	138,512	186,818
Australian Commonwealth . .	428,520	293,677	363,723	439,445	352,841	311,093	445,848	571,789
Foreign countries [1]	14,342	45,837	21,921	23,114	23,275	51,929	45,714	68,006

.The money values of the Indian exports and the countries to which the exports have taken place is given in the following table :—

---

[1] Principally Siam, Portuguese East Africa, Japan, and Dutch Guiana.

Export of Castor Seeds

Countries.	1899–1900.	1900–1.	1901–2.	1902–3.	1903–4.	1904–5.	1905–6.	1906–7.	1907–8.	1908–9.
	£	£	£	£	£	£	£	£	£	£
United Kingdom	100,130	161,320	212,187	203,762	144,859	144,970	202,909	327,803	570,303	342,873
France	142,260	167,665	180,384	172,283	82,695	82,324	113,062	137,643	130,792	146,064
Belgium	47,211	61,740	87,008	130,698	82,960	86,148	70,924	102,932	150,018	88,818
Italy	35,052	36,684	43,576	63,194	68,733	78,577	78,331	86,111	120,576	74,742
Other countries	23,769	10,401	49,457	43,774	82,057	69,040	59,226	106,639	40,179	52,972
Total	348,422	437,810	572,612	613,711	461,304	461,059	524,452	761,128	1,011,868	705,469

Countries.	1909–1910.	1910–11.	1911–12.
	£	£	£
United Kingdom	454,881	570,413	541,794
France	108,550	130,832	164,986
Belgium	123,673	149,898	141,074
Italy	102,114	127,236	126,292
Other countries	51,216	121,597	204,316
Total	840,434	1,099,976	1,178,462

The chief North American States in which castor seed is harvested are Oklahoma, (Eastern) Kansas, and (Western) Missouri. The bulk of the castor oil made in the United States is, however, derived from imported beans. The quantity of beans imported into the United States from India alone is shown in the following table, together with the amount of castor oil imported from East India :—

Imports of Castor Beans and Oil into the United States from East India

Year ending June 30,	Castor Beans.	Castor Oil.
	Bushels of 50 lbs.	Gallons.
1890	94,226	6,901
1891	105,374	2,073
1892	163,089	382
1893	147,061	286
1894	47,448	1,702
1895	277,231	28,846
1896	145,735	22,888
1897	84,128	4,368
1898	19,651	3,626
1899	25,003	7,615
1900	135,591	3,334
1901	191,288	3,206
1902	312,323	3,705
1903	380,270	6,643
1904	498,039	11,283
1910	53,707	...
1911	242,935	...
1912	777,074	...

Considerable quantities of castor seeds are also exported from Mexico [1] and Brazil. The exports from the latter country are given in the following table :—

Year.	Tons.	Year.	Tons.
1905	2646	1909	3899
1906	3126	1910	4200
1907	1221	1911	2110
1908	150	1912	753

The considerable falling off in the export is due to the fact that the consumption of castor oil in Brazil has grown, and that a number of castor oil mills have been founded, especially in the State of Pernambuco.

The seeds consist of 20 per cent of husks, rich in mineral matter but containing no oil, and 80 per cent of kernels, forming a white, softish mass. The seeds contain a toxic alkaloid " ricine." [2] They also contain a powerful fat-hydrolysing enzyme (see Vol. I. Chap. II.), which is used in a manufacturing scale for hydrolysing oils and fats for soap-making purposes (see Vol. III. Chap. XV.). The seeds contain 46 to 53 per cent of oil.

[1] Two varieties of seed are exported, one a small dark brown, mottled, and the second large, white seeds mottled with dark brown.

[2] Cp. Osborne, Mendel, and Harris, *Zeitschr. f. analyt. Chem.*, 1907 (46), 213.

Castor oil is produced on a large scale by expression or by extraction. For the best quality of oil—for medicinal purposes—the seeds are first decorticated (shelled) by being passed between rollers set at such a distance that the outer shell only is broken. The kernels are then separated from the light husks by a blast of air in a specially constructed separator. Medicinal oil can only be prepared by expression in the cold, as the "ricine" does not pass into the oil under these conditions. It is frequently stated in the literature on castor oil that this oil is used in China as a salad oil.

The once expressed cake is subjected to a second expression, followed by a third expression. The oils so obtained are unfit for medicinal use, and are employed for manufacturing purposes. The cakes (" *casto pomace*," "*castor poonac*" in India) retain the poisonous alkaloid, and are therefore unfit for use as cattle food.[1] Although attempts have been made to free the cakes from ricine by washing with 6 to 7 times their amount of a 10 per cent sodium chloride solution (*O. Nagel* [2]), no castor cake is actually being used for feeding purposes.[3] The expressed cakes (like the extracted meal, see below) are exclusively employed for manuring the land. The richness of castor cake in fertilising constituents has chiefly contributed to the growth of the castor oil industry in Marseilles, as the residual cakes are readily bought by the growers of early vegetables ("primeurs").

In India "poonac" is used principally for manure, but is also employed as fuel and for caulking timber, for the destruction of white ants and other pests, and for stuffing the soles of natives' shoes.

Next to India, Marseilles has become one of the chief centres for the production of castor oil. The importance of the castor oil and cake industry in Marseilles may be gathered from the following table :—

Imports of Castor Seeds into Marseilles

Year.			Double (metric) cwts.	Year.			Double (metric) cwts.
1896	.	.	283,960	1905	.	.	138,050
1897	.	.	149,270	1906	.	.	135,540
1898	.	.	258,880	1907	.	.	163,700
1899	.	.	259,830	1908	.	.	191,110
1900	.	.	159,420	1909	.	.	115,530
1901	.	.	259,310	1910	.	.	134,870
1902	.	.	262,140	1911	.	.	142,120
1903	.	.	215,570	1912	.	.	157,860
1904	.	.	144,070				

Since the finally pressed cake still contains about 8 per cent of oil, it is usually ground to meal, and extracted with carbon bisulphide in order to recover this amount.

[1] Cp. W. Mooser, *Landw. Versuchsst.*, 1911 (75), 107.
[2] *Journ. Soc. Chem. Ind.*, 1902, 30.
[3] With regard to the poisonous properties of castor seed, cp. Kobert, *Pharm. Zeit.*, 1906, 1062. Cp. also F. Schmidt, *Zeitschr. f. öffent. Chem.*, 1908, 245.

The imports of castor oil into the United Kingdom are detailed in the following table :—

Country of Origin.	1905.	1906.	1907.	1908.	1909	1910.	1911.	1912.
	Cwts.	Cwts.	Cwts.	Cwts.	Cwts.	Cwts.	Cwts.	Cwts.
Belgium	21,881	18,967	17,802	9,632	9,847	9,153	11,579	7,280
France	17,237	14,982	14,622	6,345	6,756	6,450	6,689	6,240
Italy	4,209	4,267	8,770	3,455	2,388	2,620	3,024	2,740
Other foreign countries .	720	245	488	713	1,258	1,810	2,875	2,020
British India . . .	17,146	11,868	13,709	11,590	12,494	6,863	13,744	8,720

The imports of castor oil into Germany during 1911 and 1912 are given in the following table :—

From	1911.	1912.
Belgium	2953	3238
France	384	294
United Kingdom . . .	5557	6321
Italy	..	451

On a large scale, about 40 per cent of oil is obtained by expression, 33 per cent being yielded by the first expression, and the remainder by the subsequent expressions. Whereas formerly most of the castor oil was obtained by expression—in fact, the whole of the castor oil exported from India is expressed oil—the process of extraction has gained ground, notably in Hull (England), and in Boston (United States). The expansion of the extraction process is, to a large extent, due to the deterioration of the Indian seed, which has occurred during the last ten years (owing to the variation of the crops, and also to insufficient attention on the part of the cultivators [1]). Hence inferior qualities are no longer used for the preparation of medicinal oil by expression in the cold, but are at once extracted with solvents. The extracted oil can, of course, only be used for manufacturing purposes.

The process of refining castor oil consists chiefly in the removal of albumen by steaming the oil. The albumen, and that part of the enzyme which has passed into the oil, are thereby coagulated, and removed by filtering. Properly refined castor oil keeps very well,[2] and does not easily turn rancid, as observations made in the author's laboratory have shown. A sample exposed to the atmosphere for four years contained only 1 per cent of free fatty acids.

Most commercial castor oil contains, therefore, only very small proportions of free fatty acids, as is evidenced by the numbers collated in the following table :—

[1] Java seed, which is properly attended to by the growers, yields therefore at present a better oil.

[2] Additional proof for this may be found in the statement made by Berthelot that the oil employed by the Egyptians for embalming was castor oil.

Free Fatty Acids in Castor Oil

Description of Oil.	No. of Samples.	Free Fatty Acids, calculated to Oleic Acid.	Observer.
		Per cent.	
Expressed oil .	9	0·68-14·61	Nördlinger
Extracted oil .	5	1·18-5·25	,,
Commercial oil	2	1·46-2·16	Thomson and Ballantyne
Indian oil	23	0·14-1·06	Deering and Redwood

Castor oil is a colourless or pale greenish oil ; its taste is at first mild, then harsh ; this harsh taste is more pronounced in American than in Italian or French oils. Contrary to older statements, it does not dry even when exposed in thin layers. A sample of medicinal oil, which the author kept exposed for four years, had its specific gravity increased from 0·9591 to 0·9629 (the iodine value had *not*, however, decreased).

The changes which castor oil undergoes on blowing with air are detailed in the following tables :—

Blown Castor Oil (Lewkowitsch)

	Original Oil.	Blown 2 Hours at 150° C.	Blown 4 Hours at 150° C.	Blown 6 Hours at 150° C.	Blown 10 Hours at 150° C.
Colour	very light	light	light	light	orange yellow
Specific gravity at 60° F.	0·9623	0·9663	0·9798	0·9778	0·9906
Acid value.	1·1	1·3	2·4	2·6	5·7
Saponification value .	179·0	182·3	185·2	184·8	190·6
Iodine value		83·5	79·63	78·13	70·01
Acetyl value	146·9	150·7	154·3	159·0	164·8
Saponification value of acetylated oil	303·9 304·3	306·5 306·0	308·3 308·7	308·3	311·0

Blown Castor Oil Fatty Acids (Lewkowitsch)

	Original Fatty Acids.	Blown 2 Hours at 150° C.	Blown 4 Hours at 150° C.	Blown 6 Hours at 150° C.	Blown 10 Hours at 150° C.
Colour	clear	yellow	dark	very dark	black
Specific gravity at 60° F.	0·9543	0·9507	0·9529	0·9525	0·9561
Acid value	174·7	149·3	128·5	112·2	93·73
Neutralisation value	176·5	173·7	177·5	177·3	181·1
Iodine value	...	86·51	86·77	85·14	85·23
Acetyl value, after removal of some solid fatty acids[1] (dihydroxystearic)	133·1	94·26	105·5	93·31	81·4
Saponification value of acetylatsd acids	299·2	284·4	272·6	272·3	264·9

The numbers obtained by *Procter and Holmes* [2] on blowing (English pressed) castor oil are as follows :—

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
Hours.			
0 [3]	0·958	1·4800	83·0
3	0·958	1·4800	83·0
6	0·958	1·4802	74·0
9	0·958	1·4804	73·0
12	0·961	1·4804	72·0
15	0·962	1·4805	71·0
18	0·965	1·4805	71·0
21	0·966	1·4806	69·0
24	0·967	1·4807	68·0

Castor oil is strongly dextro-rotatory (*Peter, Deering and Redwood*). The rotation in a 200 mm. tube varied in twenty-three specimens of Indian castor oil from $+7\cdot6°$ to $+9\cdot7°$. The optical activity is no doubt due to the presence of an asymmetric carbon atom in ricinoleic acid (cp. Vol. I. p. 213).

On standing in the cold, 3 to 4 per cent of " stearine " are deposited, consisting, according to *Krafft*,[4] of tristearin and triricinolein. *Chonowsky* [5] proposes to separate off the solid glycerides by dissolving castor oil in alcohol and allowing the solution to stand at a low temperature, when a crystalline deposit separates out. Amongst the solid fatty acids *Juillard* discovered dihydroxystearic acid (the first natural hydroxy fatty acid) to the extent of 1 per cent. The chief constituent

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[1] The acetyl value of the removed solid fatty acids was 143·3 (theory for dihydroxystearic acid : 280·5). From these acids there was obtained an acid of the melting point 180° C. (melting point of dihydroxystearic acid 131° C.), insoluble in petroleum ether.

[2] *Journ. Soc. Chem. Ind.*, 1905, 1287.

[3] Original castor oil.

[4] *Berichte*, 1888, 2730.

[5] *Berichte*, 1909, 3341.

of castor oil is triricinolein. Triricinolein is, according to *Krafft*, solid in its pure state ; and the liquid state of castor oil would have accordingly to be ascribed to a state of superfusion of the oil. *Hazura and Grüssner* stated that the liquid fatty acids from castor oil consist of ricinoleic and isoricinoleic acids ; *Krafft's* solid acid is, perhaps, identical with one of these acids (cp. also Vol. I. p. 215, *Mangold*). Olein does not occur in castor oil.[1] Castor oil would therefore consist in the main of the glyceride of ricinoleic acid, all the isomerides being comprised under that term.

The occurrence of stearic acid, ricinoleic acid, and hydroxystearic acid in castor oil has been confirmed by *A. Haller*.[2] He was, however, unable to confirm *Hazura and Grüssner's* statement as to the occurrence of two isomeric ricinoleic acids in castor oil (cp. Vol. I. p. 215).

The proportion of triricinolein calculated by the author from the (mean) acetyl value of castor oil, 150, would be—as the acetyl value of triricinolein is 159·1 (Vol. I. p. 430)—$\frac{150 \times 100}{159\cdot1} = 94\cdot28$ per cent ricinolein ; since dihydroxystearic acid—present to an extent of 1 per cent amongst the fatty acids—has the acetyl value 280·5, the percentage of ricinolein can only be about 93. The iodine value of triricinolein being 81·76, the above calculated 93 per cent of triricinolein would absorb 76 per cent of iodine. Castor oil must therefore contain some less saturated fatty acids than ricinoleic. This is indeed borne out by the iodine value of the liquid fatty acids, viz. 106·9.

By catalytic reduction of castor oil with hydrogen in the presence of colloidal palladium in the cold, *Paal and Roth*[3] obtained a solid fat softening at 69° C., melting at 77° C., and having the iodine value 1·9. Catalytic reduction with nickel readily yields a solid product. Having regard to the behaviour of ricinoleic acid in the catalytic process (cp. Vol. I. p. 214), it will be easily gathered that hydrogenated (hardened) castor oil may have retained its original acetyl value, or have lost it to some extent, or entirely, according as the hydroxyl group has been eliminated completely or partially in the hydrogenising process. Hydrogenated castor oil which has practically lost the hydroxyl group entirely, is insoluble in alcohol, having become converted into stearin. Hydrogenated castor oil which still retains the hydroxyl group is soluble in alcohol, and behaves with petroleum ether very much like natural castor oil.

The amount of unsaponifiable matter in castor oil fluctuates between 0·30 and 0·57 per cent.

The specific gravity of castor oil, its behaviour with solvents, its acetyl value, and its very high viscosity afford ready means of identification.

Castor oil has the highest *specific gravity* of any natural fatty oil ; only the " blown oils " (Vol. III. Chap. XV.) acquire so high a gravity in

[1] Hazura and Grussner, *Journ. Soc. Chem. Ind.*, 1888, 681.

[2] *Compt. rend.*, 1907 (144), 462.

[3] *Berichte*, 1908, 2283 ; 1909, 1543. Cp. also French patent 434,927 (*Vereinigte chemische Werke*).

the course of manufacture. Hence the presence of a foreign fatty oil in castor oil would, in the first instance, be recognised by a lower gravity of the sample than 0·960. Rosin oil of specific gravity 0·998, which may have been added to an adulterated oil in order to mask the influence of a foreign fatty oil, can be easily detected by determining the unsaponifiable matter quantitatively.

Castor oil has the highest *viscosity* of all known natural fatty oils, only " blown oils " (Chap. XV.) and rosin oil approaching it in this respect. The viscosity of the twenty-three samples examined by *Deering and Redwood* was from 1160 to 1190 seconds for 50 c.c. at 100° F.

Castor oil is miscible in every proportion with glacial acetic acid and absolute alcohol. It also dissolves, at 15° C., in 2 volumes of 90 per cent, and in 4 volumes of 84 per cent alcohol. *Van Itallie*[1] determined the solubility, in 90 per cent alcohol, of five samples of castor oil, with the following result :—

10 c.c. of Oil.	Require 90 per cent Alcohol at 20° C. c.c.
A expressed at 20° C. .	26·4
B ,, ,, 50° C. .	26·8
C ,, ,, 80° C.	27·8
D commercial oil	29·4
E ,, ,,	24·0

For the rapid examination of castor oil (by custom-house officers), *Finkener*[2] recommends agitation of 10 c.c. of the sample with 50 c.c. of alcohol of the specific gravity 0·829 at 17·5° C., in a graduated cylinder. A strong turbidity, which does not disappear even at 20° C., shows that the oil is not pure ; even 10 per cent of foreign oils (sesamé, linseed, rape, cotton seed oils) may thus be detected.

Castor oil is nearly insoluble in large quantities of petroleum ether, kerosene, and higher boiling paraffin oils ; as little as 0·5 per cent of castor oil causes a turbidity at 16° C. However, castor oil gives a homogeneous solution with an *equal* measure of petroleum ether, or one volume and a half of kerosene or paraffin oil ; if more of the solvents is used, the excess floats on the top of the mixture. The characteristic insolubility is lost at the ordinary temperature if castor oil be adulterated with a small quantity of another fatty oil.

Castor oil is distinguished from all other oils—with the exception only of grape seed oil (pending further examination of grape seed oil) by its high *acetyl value*. In the case of castor oil the acetyl value is an important " characteristic." Its determination furnishes, therefore, the surest means of ascertaining purity, and enables the analyst to estimate the amount of adulteration.

The saponification value (approaching that of the oils belonging to the rape oil group) and the *iodine value* also afford means of detecting fraudulently added oils.[3]

[1] *Chem. Zeit. Rep.*, 1890, 367.
[2] *Journ. Soc. Chem. Ind.*, 1887, 148.
[3] The saponification and iodine values given by Thörner, viz. 201·203 and 93·94 respectively are so abnormal that I have omitted them from the table of characteristics.

Physical and Chemical Characteristics of Castor Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. 1/10 norm. KOH.	Observer.
15·5	0·9591 [5]	Lewkowitsch	– 10 to – 12 [2]	Schaedler	180-183	Itallie	84·4	Hühl	1·1 [7]	Lewkowitsch
,,	0·9653-0·9679	Thomson and Ballantyne			178·6-180·2	Thomson and Ballantyne	83·6-83·9	Thomson and Ballantyne		
,,	0·9637-0·9642	Deering and Redwood [1]			176·7-179·1	Deering and Redwood [1]	83·7-85·3 [4]	Deering and Redwood [1]		
20	0·9589	Long			185·9-186·6	Honriques [3]	86·2-87·1	Wijs		
	0·963-0·965	Itallie			183·3 [5]	Lewkowitsch	81·4-90·6 [6]	Lewkowitsch		
25	0·9555	Long								
30	0·9522	,,								
35	0·9488	,,								
99	0·9096	Allen								
(water at 15·5=1)										

[1] Twenty-three samples of Indian oil, *Journ. Soc. Chem. Ind.*, 1894, 959.   [2] American oil, which is richer in solid glycerides than Indian or Italian oil.   [3] Java oil.   [4] Calculated from bromine values, 52·8-53·7.   [5] Calcutta oil, second pressing.   [6] Medicinal oil.   [7] This number must not be accepted as being generally applicable.

Physical and Chemical Characteristics of Castor Oil—continued

Acetyl Value		Thermal Tests				Refractive Index			Viscosity in Redwood's Viscometer	
		Maumené Test		Heat of Bromination						
Observer.		°C.	Observer.	°C.	Observer.	At ° C.		Observer.	Seconds at 100° F.	Observer.
Lewkowitsch	149·9	47	Maumené	15	Helmer and Mitchell	15	1·4795-1·4803	Strohmer	1160-1190	Deering and Redwood
„	150·5	46	Archbutt	14·7	Jenkins	20	1·4783-1·4789	Harvey		
						60	1·4636	Thorner		

Specific Temperature Reaction: 89-92   Thomson and Ballantyne

Oleo-refractometer.

"Degrees" at 22° C.	Observer.
+43 to +46 [1]	Jean
+ 37	Bruyn and van Leent
+ 40	„ „
+41 to +42·5	Deering and Redwood
+39 to +42	Pearmain

Butyro-refractometer.

At ° C.	"Degrees."	Observer.
25	78	White
40	65·5	„

[1] Java oil.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity		Solidifying Point		Melting Point		Mean Molecular Weight		Iodine Value		Refractive Index	
At °C.	Observer	°C.	Observer	°C.	Observer		Observer	Per cent.	Observer	At 60° C.	Observer
15·5	Allen	3	Hübl	13	Hübl	290-295	Alder Wright	86·6-88·3	Morawski and Dennsi	1·4546	Thorner
0·9509											
98-99	,,					306·6	Allen	87-88	Thorner		
0·8960											
								Liquid Fatty Acids.			
								106·9[1]	Tortelli and Ruggeri		

[1] Italian oil, 1898 crop; iodine value of oil, 87·4.

In the *elaïdin test* castor oil gives a whitish solid mass, due to the formation of ricinelaïdin.

On nitrating castor oil with concentrated nitric and sulphuric acids, " nitrated " castor oil is obtained (cp. Vol. III. Chap. XV.).

If the price of castor oil is low, adulteration with a fatty oil will hardly be practised. When castor oil was high in price, adulteration with rape oil, rosin oil, and chiefly with blown oils, did occur.

Rosin oil is easily detected by determining the unsaponifiable matter. Obviously, the polarimetric examination of the sample would be useless if rosin oil be present.

The " blown oils," although simulating castor oil in specific gravity and viscosity, differ from it in having much lower acetyl values, higher saponification values (see Chap. XV.), and lesser solubilities in alcohol.

Castor oil in other oils is easily detected by the high acetyl value and the high specific gravity of the sample.

Castor oil is used in medicine (the purgative action of the oil is due to ricinoleic acid). Recently attempts have been made to convert castor oil into medicinal preparations, having the form of powders (see Vol. III. Chap. XV.). Up to the year 1877 the only outlet for castor oil was in pharmacy. After that year the employment of castor oil for the manufacture of Turkey-red oils (" alizarine assistant "), " Emulsified Oils " (Vol. III. Chap. XV.), commenced to gain in importance. On sapouification with soda, castor oil (like cocoa nut oil) yields a hard soap which requires very large quantities of salt for " salting " out. It is therefore little used alone in the manufacture of hard soaps. The soda soap has, however, the property of imparting transparency to soaps ; hence castor oil is extensively employed in the manufacture of transparent soaps.

In India the oil is largely employed as a lubricant for locomotive bearings. In this country it is too thick to be serviceable for this purpose. It is, however, used for lubricating marine engines, and for the manufacture of blended lubricating oils (cp. also Vol. III. Chap. XV.).

Castor oil is used also as a preservative for leather belting in heavy work, and for fat liquoring in the leather industries. It also plays an important part in the preparation of fly-gums, and in the manufacture of other adhesive agents.[1] Castor oil has been proposed as a substitute for camphor in the manufacture of celluloid,[2] and as a solvent of sulphur for pharmaceutical purposes.[3]

On a smaller scale castor oil is subjected to destructive distillation for the preparation of " cognac oil," when undecylenic acid and œnanthaldehyde pass over, whilst the remaining mass solidifies to a very bulky, spongy, india-rubber-like mass, for which a solvent has not yet been found.[4] The residue, after successive washings with alcohol, chloroform, and ether, was found to have the composition[5] $C_{33}H_{58}O_5$,

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[1] Cp. Castle, English patent 6936, 1905 ; Patat and Co., French patent 361,954 (gum tragasol and castor oil).

[2] C., Gillet, French patent 382,270.

[3] *Oleum Ricini sulfuratum* ; cp. Schelenz, *Pharm. Zeit.* (57), 473.

[4] *Berichte*, 1876, 2034.

[5] Fendler and Thoms, *Arch. d. Pharm.*, 1901 (239), 1.

corresponding to the anhydride of triundecylenic acid, $(C_{11}H_{20}O_2)_2-H_2O$. On melting the product with potassium hydroxide, it yields a hexa-undecylenic acid, $C_{16}H_{30}O_2$. By oxidation with fuming nitric acid, sebacic acid and an acid of the formula $C_{13}H_{22}O_4$ were obtained; by oxidation with potassium permanganate, sebacic acid and lower fatty acids were produced. If the distillation of castor oil be stopped just before the mass would have become converted into the india-rubber-like substance, the oily residue still contains glycerides. This residue corresponds to the composition $C_{105}H_{148}O_{18}$, which appears to be the glyceride of the dibasic triundecylenic acid :—$(C_3H_5)_2(C_{33}H_{58}O_6)_3$ (cp. Vol. III. Chap. XV. " Polymerised Oils ").

Castor oil is also polymerised by heating for 10 hours to 260°-300° under a pressure of 4-6 atmospheres ; its product is miscible with mineral oils.[1]

Lesser known non-drying oils, see table opposite.

2. ANIMAL OILS

The fatty oils obtained from animals are described in this section under the following two classes—

(1) Marine animal oils,
(2) Terrestrial animal oils.

This subdivision is not made merely for the sake of convenience ; it is based on striking chemical differences. Broadly speaking, these two groups may be compared with the two large classes of vegetable oils, viz. the drying and the non-drying oils.

Like the drying oils the marine animal oils are characterised by very high iodine values, by the large amount of ether-insoluble bromides they yield, by their power of absorbing oxygen, and by the feature that they do not yield elaïdins.

The majority of the terrestrial animal oils resemble the non-drying oils in that they have low iodine values, do not easily absorb oxygen, and yield solid elaïdins.

Just as vegetable oils exist which occupy an intermediate position between the drying and the non-drying oils, viz. the semi-drying oils, so we find among the *marine* animal oils gradations from the most pronounced type of readily oxidisable oils to those containing large quantities of glycerides of saturated fatty acids, thereby approaching the chemical constitution of terrestrial animal oils.

Similarly, such intermediate oils may be expected amongst the oils from *terrestrial* animals. Hitherto, only one oil—chrysalis oil—has been described somewhat fully. It may be looked upon as a representative of semi-drying animal oils (cp. also " Drying Animal Fats " and " Semi-Drying Animal Fats ").

[1] English patent 24.935, 24,936, 1905.

Oil fr	Saponition V	Iodine Value.	Refractive Index.	Observer.
Horse chestn	19 quid	95·8		M. Stillesen [1]
	20	..	.	J. J. C. Bakker [2]
Oleander		..		J. J. Camo [3]
Toad-stool		..		Hennisch and Zellner [4]
Louc-Mouc t		..		Millian [5]
Birch seed	21	..	.	Lidoff [6]
	19	..		Niederstadt [7]
Parsley seed	19			Vongerichten and Köhler [8]
Ungnadia	19	86-87	..	Schaedler [9]
Fenugreek	18	79·8	1·4626 (40°)	Grimme
Lucerne	19	77 8	1·4659 (40°)	,,
Yellow clov	18	78 3	1·4666 (40°)	,, [10]
White clov	18	68 1	1·4624 (40°)	,,
Bastard cl·	18	69 5	1·4626 (40°)	,,
Red clover	19	66·0	1·4626 (40°)	,,
Pink clove	18	66·1	1·4620 (40°)	,,
	20	73 4	..	Menon [13]
	20	75·3	.	,, [11]
	20	83·1	.	
White Mel	18	74 8 (!)	1·4812 (50°)	Grimme [10]
Melilot .	19	64·7	1·4659 (50°)	,,
Horn tref	19	73·4	1·4620 (45°)	,,
Wound w	18	79·7	1 4640 (45°)	,,
Turkish d	17	75 9	1 4574 (50° C.)	,, [10]
Bird's foo	18	..	1 4593 (50° C.)	,,
Blue Lup	18	67 6 (!)	1·4566 (50°)	,, [10]
Yellow L	18	64 0	1 4600 (50°),	,, [10]
White Lu	19	56 3	1 4559 (50° C.)	,, [10]
Lag wort	17	62 0	1·4672	,, [10]
Soap tree	17	..	..	O. May [16]
	19	57 0		Menon [13]
Sedge	22	..	..	W. Hopfner and H. Burmeister [18]
Cashew n	16	..	..	Niederstadt
Coula, K	..	..	..	Lecomte and Hébert [19]
Kô-sam s	..	..	..	Power and Lees
	18	.	..	Power and Salway [21]
Spice bus	28	..	..	Caspari [23]
bush se				
	20	..	..	Frankforter and Martin [25]
Apeiba, E	23	34·5	..	Lewkowitsch [26]
Elm seed	27	..	..	Pawienko [27]

[1] Chem
S. J. M. A
[2] Phar der
[3] Bull
[4] Mone
per cent of
90 per cent by
authors for
Reichert-M (!!),
index at
mushroom
tharellus a
flava, Lyc un-
Tramites stearic
and contai
at 74° C.
[5] Jour

meter.
ourn., 1902, 291. Melting point of oil, 26° C. ; Reichert value,
is stated to consist of the glycerides of capric, lauric, and oleic
erating.
t yellow, has a pleasant taste and a characteristic odour. The
C. is 0·9312, and at 20° C., 0·9203. The refractive index at 0° C.
° C., 1·48228. The husks yielded to ether 8·5 per cent of a black
c gravity 0·9412 at 20° C. and 0·933 at 35° C. This oil has the
79·7, and the iodine value 87·2.
Pharm., 76, 151.
value, 7·75. Titration number insol. volatile fatty acids, 27·21.
Rs, 10·2 per cent of mean molecular weight, 167·8 (Compt. rend.
m. des Sciences, 1909, 356).
1912, 43 ; Reichert value, 3·75. The mixed fatty acids contain
r cent of capric acid. The statement that the oil contains also
accepted with reserve.

(1) MARINE ANIMAL OILS

The members of this class are conveniently subdivided into the following three groups :—

a. Fish oils.
β. Liver oils.
γ. Blubber oils.

The term " train oil " is avoided in this work, as its German equivalent " Tran " includes all three groups, and therefore causes unnecessary confusion. It must further be premised that, under *blubber oils,* only those oils are included which consist wholly or in greater part of glycerides. Therefore the liquid waxes—viz. sperm oil and Arctic sperm oil, which are frequently classed together with blubber oils—are excluded from this group.

The oils belonging to " Marine Animal Oils " are liquid at the ordinary temperature ; on cooling they yield, however, varying amounts of solid glycerides. They are readily distinguishable from other liquid fats by their fishy taste and smell.

The specific gravities of the marine animal oils vary between 0·916 and 0·930.[1] The saponification values of some of the blubber oils deviate widely in both directions from the mean value of the majority of vegetable and marine animal oils—195—according as they contain, on the one hand, large amounts of spermaceti, or glycerides of volatile fatty acids on the other. Hence this characteristic cannot be used as a basis for subdivision.

The liver oils appear to form a natural group characterised by the presence of notable amounts of cholesterol and, owing to their origin, also small amounts of foreign substances. Since, for the purposes of subdivision, the iodine value is adopted in this work as the basis, the liver oils are interposed between the fish oils and the blubber oils.

The earlier statements that the marine animal oils are characterised, and can be differentiated from all other fatty oils, by the intense colourations they give with caustic soda, sulphuric acid, nitric acid, and phosphoric acid, must be considered as valueless.

Phosphoric acid, in particular, was proposed as a very characteristic reagent, capable of detecting even 0·1 per cent of these oils if admixed with vegetable oils. The best results were stated to be obtained by warming five measures of the oil under examination with one volume of syrupy phosphoric acid, when all oils belonging to this class, both alone or in admixture with other oils, showed intensely red, reddish-brown, or brownish-black colourations. *Holde* [2] indicated that the phosphoric acid test was uncertain, as on the one hand rosin oils produce red colourations with this acid, and on the other hand distinct coloura-

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[1] For some comparative viscosities of fish oils see G. F. White, *Les Matières grasses,* 1912, 2677, 2719.

[2] *Journ. Soc. Chem. Ind.,* 1890, 419.

tions only appear when large quantities of marine animal oils are present in other oils. The author,[1] after an exhaustive examination of these colour reactions, has come to the conclusion that they are by no means characteristic of these oils, but are due to impurities which can be removed by proper modes of refining. Thus, a sample of horses' foot oil (not refined), prepared in the author's laboratory, gave, with the above-mentioned reagents, colourations which might be considered as typical of marine animal oils. *Old* samples of linseed and cotton seed oils behaved similarly.

The same conclusion holds good of the chlorine test (cp. Vol. I. p. 495).

Owing to the large amount of unsaturated fatty acids which the marine animal oils belonging to this class contain, they develop a considerable amount of heat in the thermal tests.

The nature of the fatty acids in these oils is still very imperfectly known. Some of the blubber oils have high *Reichert* values, pointing to the presence of large quantities of volatile acids. Others deposit "stearine." On cooling this appears to consist chiefly of palmitin. Most of these oils contain large proportions of unsaturated fatty acids, as is shown by their high iodine values, ranging from 120 upwards and approximating the values characteristic of perilla and best linseed oils. The high iodine values, especially those of the fish and liver oils, clearly point to the presence of acids much less saturated than those belonging to the oleic series. It is by no means certain that oleic acid occurs in these oils. The "physetoleic" acid of the earlier authors (cp. Vol. I. p. 177) could not be detected by *Fahrion*.[2] *Bull's* [3] statement that all oils belonging to this class—with the exception of cod liver oil—contain erucic acid, as also an acid of the formula $C_{20}H_{38}O_2$, still requires confirmation to some extent ; all the more so, as *Bull* [4] later on showed that erucic acid does occur in cod liver oil (see below), and as the several highly unsaturated acids mentioned by him could not be detected by *Tsujimoto* (see below). The unsaturated acids cannot be identical with linolic or linolenic acids, as the oils, although absorbing large amounts of oxygen, do not dry like linseed oil with the formation of a flexible skin. The fish oils proper dry better than the liver oils, the best of them being menhaden, sardine, and herring oils. These oils when used alone dry to a somewhat sticky skin. The author observed many years ago that the free fatty acids from seal and cod liver oils kept in stoppered glass bottles deposit, after a few months' standing, a resinous substance. *Tsujimoto* [5] following up this observation discovered in a large number of fish, liver, and blubber oils clupanodonic acid (Vol. I. p. 210) to an extent of from 6 to 9 per cent. Owing to the presence of this acid the marine animal oils yield in the bromide test considerable amounts of brominated glycerides. These differ from the ether-insoluble bromides obtained from vegetable drying oils (cp. Vol. I. p. 475). The ether-insoluble bromides prepared from the mixed fatty acids do not melt, like linolenic

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1894, 617.   Cp. Vol. I. Chap. VII.
[2] *Journ. Soc. Chem. Ind.*, 1893, 938 ; 935.   [3] *Chem. Zeit.*, 1899, 996.
[4] *Berichte*, 1906. 3570.   [5] *Chem. Revue*, 1913, 70.

[ether-insoluble] bromide, at about 175°-180° C., but remain solid up to about 200° C., and then become black, without, however, melting to a liquid (cp. Vol. I. p. 571).

. *Tsujimoto* [1] examined similar resinous substances obtained from Japanese sardines, herring, and whale oils after three years' standing. They were insoluble in petroleum ether, ether, and carbon-tetrachloride. Undoubtedly these resinous substances represent " oxidised acids." The elementary analysis published by *Tsujimoto* favours the view that they are oxidation products of clupanodonic acid. Indeed, the rapid oxidation which the free fatty acids of fish, liver, and blubber oils undergo, is characteristic of these oils and seems to be due to the presence of clupanodonic acid. Hence old marine animal oils—and even those which have been bleached by sunlight—give dark-brown soaps, whereas freshly prepared oils give only slightly coloured soaps. The changes which the oils undergo by insolation are evidenced by the following table :—

	Japanese Sardine Oil.		Herring Oil.	
	Before Exposure to direct Sunlight.	After Exposure to direct Sunlight.	Before Exposure to direct Sunlight.	After Exposure to direct Sunlight.
Colour	Brownish yellow	Pale yellow	Reddish yellow	Pale yellow
Odour	Fishy	Distinctly changed	Fishy	Distinctly changed
Consistence	..	Very viscous	..	Very viscous
Specific gravity 15° C. . .	0·9359	0·9672	0·9243	0·9446
Acid value	10·02	11·08	2·58	2·61
Saponification value . .	196·34	215·65	183·97	196·38
Iodine value (Wijs) . .	176·78	134·89	118·62	96·39
Refractive index 20° C. . .	1·4804	1·4838	1·4757	1·4772
Ether - insoluble bromide, per cent	43·40	24·46	21·20	10·71
Oxidised acid	0·27	8·63	0·92	5·62

Fahrion [2] is of opinion that he has proved the presence of an unsaturated acid, $C_{18}H_{30}O_2$—jecoric acid—(cp. Vol. I. p. 209), and infers the presence of an unsaturated acid of the composition $C_{17}H_{32}O_2$ —asellic acid—from a dihydroxylated acid (dihydroxyasellic acid) obtained on oxidising the fatty acids of sardine oil. In the light of *Ljubarsky's* statement (Vol. I. p. 227, " Dihydroxypalmitic Acid ") that dihydroxystearic acid forms with dihydroxypalmitic acid a " eutectic " compound, the existence of dihydroxyasellic and hence of asellic acid itself must be doubted. *Heyerdahl* claimed to have discovered two unsaturated acids in cod liver oil, viz. jecoleic and therapic acids (Vol. I. p. 194 and p. 210). *Bull* assumes amongst the liquid fatty acids of cod liver oil the presence of an acid of the com-

[1] *Journ. Coll. Eng. Tokyo Imp. Univ.*, 1908, iv. 193.
[2] *Journ. Soc. Chem. Ind.*, 1893, 935.

position $C_{23}H_{36}O_2$, belonging to the series $C_nH_{2n-10}O_2$. The existence of all the last-mentioned acids is so far hypothetical. An investigation of this subject was therefore a desideratum.

Tsujimoto doubts the occurrence of jecoric acid in herring oil, and has further shown that no evidence could be obtained of the presence of the two highly unsaturated acids of the formulæ $C_{22}H_{32}O_2$ and $C_{24}H_{40}O_2$, stated by *Bull* to occur in herring oil. The existence of *Bull's* [1] gadoleic acid, $C_{20}H_{38}O_2$ (Vol. I. p. 194), also stands in need of confirmation.

The "Bromide test," described Vol. I. p. 475, can be used as a qualitative test for the detection of fish, liver, and blubber oils by filtering off the ether-insoluble brominated glycerides and subjecting them to the melting-point test. By proceeding as described in Vol. I. p. 570, the test can be made a quantitative one.

Halphen [2] recommends as a qualitative test for the presence of marine animal oils, a reagent consisting of 28 volumes of glacial acetic acid, 4 volumes of nitrobenzene, and 1 volume of bromine, which differs from that employed in the bromide test merely by the presence of nitrobenzene. Evidently *Halphen's* method does not admit of a differentiation of marine animal oils from vegetable drying oils. The same stricture holds good for the further suggestion made by *Halphen*, viz. to differentiate the ether-insoluble bromides obtained from linseed oil, from those yielded by marine animal oils, by their behaviour with boiling carbon tetrachloride. Experiments made in the author's laboratory proved that the ether-insoluble bromide from linseed oil does dissolve in hot carbon tetrachloride, and gives a somewhat crystalline precipitate on cooling, whereas the ether-insoluble bromide from marine animal oils does not dissolve completely and gives a gelatinous precipitate on cooling. It would, however, be impossible to differentiate thus linseed oil from marine animal oils ; it is still more hopeless to detect thus marine animal oils in linseed oil. The different behaviour in the melting-point test of the ether-insoluble bromides of the mixed fatty acids is so characteristic that *Halphen's* solubility test is superfluous.

a. Fish Oils

The fish oils are obtained from all parts of common fish—such as the herring, sardine, salmon, sprat, etc.—by boiling with water. The livers of these fish contain, as a rule, very little oil, whereas the bodies of the liver-oil-yielding fish, notably cod fish, yield so little oil, that it is not prepared commercially. Cod fish only contains 1·8 per cent, and ling fish 2·2 per cent of oil.[3]

It should be noted that the industry of fish oils has undergone a very important change during the last decade, in consequence of the

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[1] *Berichte*, 1906, 3574.   [2] *Journ. Pharm. Chim.*, 1894, 359, 391.
[3] Greshoff, *Chem. Zeit.*, 1906, 856.

replacement of fishermen's sailing boats by steam trawlers and more recently by motor boats. Whereas in former times fishing boats would remain out at sea for about a week or two, the fish are at present brought to shore (*i.e.* into the rendering establishment) almost within one day.[1] Thus deterioration due to the oil having remained for some time in contact with highly putrescible matter has been obviated to a large extent. The very dark colour and rank odour which used to characterise fish oils has therefore given place to a somewhat paler colour and a much less unpleasant, though still strongly pronounced, fishy smell. Oils so obtained lend themselves readily to refining operations ; it may, however, be mentioned that special processes applied by the author on a large scale to oils of rank odour have brought even these oils within the reach of industrial application.

In consequence of these improvements, and the erection of establishments in which rendering is conducted on such a large scale that the separation of livers from the bodies of oil-yielding fish is performed more carefully, commercial fish oils are now comparatively free from liver oils, which were so prevalent in the fish oils of former years. The analytical numbers published by earlier observers frequently referred to a mixture of fish and liver oils, a fact which explains the large amount of unsaponifiable matter stated to occur in fish oils. These unsaponifiable matters were due to the presence of liver oils, as also of liquid and solid waxes, which were intermixed with the fish oils. Hence those numbers which appeared to the author unreliable have been omitted from the following pages.

Many attempts have been made to deprive the fish oils of their peculiar fishy taste, and to bring them within the range of edible oils.[2] All these endeavours have failed hitherto, but the tempting nature of the problem is still attracting the attention of inventors. *A. de Hemptinne* patented a process [3] for treating fish oils with ozone, with a view to removing their peculiar taste. I can state from my own experience with samples treated by this process, that it does not appear unpromising, but hitherto oils so treated have not appeared on the market. *Welfling* [4] as also *van der Heyden* [5] suggest to deodorise fish oils by extraction with alcohol, followed by filtration over char, fuller's-earth.

Less deserving of attention are the processes aiming at the treatment of fish oils or their fatty acids with concentrated sulphuric acid,[6] or with sulphuric acid and sodium nitrate.[7] *E. Bohm* [8] claims to deodorise fish oils by heating them *in vacuo* to a temperature of 350° to 400° C. *E. Petersen and H. Holstein* [9] treat with superheated steam

[1] (Petrol) Motor boats in sardine fishing.
[2] Cp. Lewkowitsch, "Problems in the Fat Industry," *Journ. Soc. Chem. Ind.*, 1903, 592., Cp. also Vol. III., "Edible Oils."
[3] English patent 12,525, 1905 ; German patent 169,410.
[4] French patent 394,456.   [5] French patent 394,530.
[6] Sandberg, German patent 162,638 ; French patent 329,256 ; English patent 2202, 1903.
[7] Potolowsky, United States patent 823,361.   [8] English patent 7901, 1906.
[9] German patent 202,576, 1908 ; Norwegian patent 18,305, 1907.

and char and chalk. *Bottaro* [1].states that odourless fish oil fatty acids are obtained by saponification with lime and by decomposing the lime soap with sulphurous acid.[2]

Tsujimoto [3] attributes the fishy odour of marine animal oils to the presence of the glyceride of clupanodonic acid, and states that in order to deodorise the oils this glyceride must be either removed, or its constitution altered.   It should be noted that on hydrogenating fish oils by means of a catalyst the characteristic fishy odour disappears.

Panzer [4] has shown that the flesh of fish which has been packed in ice contains a considerable amount of indol, and ascribes to this its peculiar smell.   Attempts have been made to deodorise fish oils by means of the action of dilute sulphuric acid and 0·2-0·5 per cent of zinc dust.   For the detection of fish oils in animal or vegetable oils the bromide test (Vol. I. p. 475) should be applied to the liquid fatty acids prepared by the lead-salt-ether method (see Vol. I. p. 545), great care being taken to avoid oxidation during their isolation.   The melting point of the bromide shows at once if any fish oil is present. If the bromide does not melt it should be extracted with boiling benzene, when the hexabromide will pass into solution leaving the pure octobromide undissolved.   The saturated fatty acids should be examined for erucic acid by hydrogenating and subsequently isolating behenic acid (see Vol. I. p. 555).

The chief centres of the fish oil industry are the northern ports of the east and west coasts of Great Britain, Gloucester on the east coast and San Francisco on the west coast of the United States, and the east and west coasts of Canada.   Japan is at present making great efforts to place its fish oil industry on a proper commercial basis. Smaller quantities of oils are furnished by the sardine packing works, in which sardine oil is prepared as a by-product, and by some minor installations, such as an establishment in Alt-Pillau (East Prussia), where miscellaneous fish caught in the Baltic are worked up by maceration between rollers, drying of the comminuted mass, and extraction with " benzine."

If fish oils are allowed to stand for some time, especially at low temperatures, larger or smaller quantities of " stearine " separate. This " stearine " (" fish stearine ") is collected separately (cp. Vol. III. Chap. XVI.).

[1] English patent 23,534, 1906 ; German patent 230,123. Cp. also E. Marks, English patent 17,430, 1912 ; C. Welfling, French patent 394,456 ; G. van der Heyden, French patent 394,530.
[2] Cp. also Hofman, Belgian patent 260,360 ; Oelwerk, Berlin G.m.b.H. ; Italian patent 409/133/132,238.
[3] *Journ. Coll. Eng Tokyo Imp. Univ.*, 1908, 177.
[4] *Chem. Zeit.*, 1909, 1016.

MENHADEN OIL

French—*Huile de menhaden ; Huile d'Alose.*   German—*Menhadenöl.*
Italian—*Olio di menhaden.*

For table of characteristics see p. 414.

Menhaden oil is an American fish oil, and, like other fish oils, is prepared from the body of fish, especially from that of the menhaden, *Alosa menhaden,* Cuv. (*Brevoortia tyrannus*), a fish somewhat larger than a herring. From about May until November this fish appears in enormous quantities off the Atlantic coast (especially off New Jersey), so that as much as 400,000 tons are caught in one season. A century ago it was part of the duties of the farmer along the Atlantic coast to devote some weeks in each year to catching menhaden fish for use as a fertiliser.

The fish are delivered from the steamers, by means of elevators, on to automatic conveyors, from which they are passed over automatic scales into large boiling pans. These are provided with false bottoms, below which open steam coils are fixed. On boiling the contents of the pan the fish are disintegrated and the oil separates easily from the flesh. After turning off the steam and allowing the mass to rest, the oil rises to the top and can be skimmed off by means of swivel skimmers.[1]

During the last few years boiling vessels have been introduced which permit of continuous working, the fish being passed on conveyors through the boilers,[2] whilst open steam acts on the fish. The time required for the fish to pass through the boiler, lasts from fifteen to twenty minutes. The whole mass is then transported by screw conveyors into settling tanks, where the oil separates by gravitation. In either process the " fish scrap " falls to the bottom of the vessels, and is then pressed in hydraulic presses, similar to those used in the working up of " tankage " (see Vol. III. Chap. XVI.), when a further quantity of oil—inferior in colour—is obtained. In some works such pressed cake—termed " chum "—is boiled out with hot water and pressed once more ; but this process is not carried out in large works, as it is not remunerative, the fish only containing from 1 to 16 per cent of oil (cp. Vol. II. Chap. XIII.) The scrap is finally dried in continuous dryers, of which various types are in use (*Anderson* dryer, *Cummer* dryer, vacuum dryers), and is sold as a valuable manure.[3] In fact the " scrap " was formerly considered as the main product, and it is owing to the demand for scrap that the fish oil industry has assumed such large dimensions.

[1] Cp. French patent 416,558. Lange, Pujol and Delpon.
[2] Cp. English patent 25,425, 1901, F. V. Speltie, and German patent 151,553, F. V. Speltie ; cp. also French patent 338,472, " Procédé et appareil pour la fabrication continue d'huile de poisson et de guano," H. J. A. Pompe van Meerdeervorte ; German patent 135,566, Ch. Wacker ; English patents 24,604, 1901 ; 18,743, 1902, E. R. Edson (in the name of Haddon). German patents 139,969 ; 141,595, 149,613, E. R. Edson. German patent 168,132, P. Hagen. English patent 25,882, 1906, Pearson.
[3] Cp. C. Kippenberger, *Zeitschr. f. angew. chem.,* 1913, 154. Cp. also V. Cambon, Portuguese patent 7801, 1911.

With the extension of the industry, new uses have been found for the oil itself, which ranks equal in value to the scrap, but fetches a much higher price when the price of linseed oil is high.[1]

In order to show the extent of the menhaden fish oil industry the following table, published by the United States Fish Commission of Washington, is given :—

State.	Year.	No. of Works.	Number of Fish worked up, in Thousands.	Oil Produced.		Fish Scrap Produced.		Value of Total Production.
				Gallons.	Value in Dollars.	Tons.	Dollars.	Dollars.
Connecticut } New York }	1912	8	317,405,700	3,613,500	838,216	28,374	484,303	1,322,519
New Jersey } Delaware }	1912	7	148,517,400	957,337	247,831	12,766	252,339	500,170
Virginia	1912	20	511,061,050	1,907,083	426,948	40,255	1,208,321	1,635,269
North Carolina } Florida }	1912	13	84,859,600	173,283	38,995	7,125	193,202	232,197
Total		18	1061,843,750	6,651,203	1,551,990	88,520	2,138,165	3,690,155

The colour of menhaden oil varies according to the state of freshness in which the fish arrives, and with the duration of the boiling process. The longer the oil has been allowed to remain in contact with the putrescible mass and the longer the fish has been boiled, and hence the longer the oil has been in contact with the gluey water, the darker is its colour. Therefore, the separation of the oil from the gluey water is carried out as rapidly as possible. Fresh fish yield a light coloured oil ; the oil running from the " scrap " in the presses is the darkest in colour.

In commerce the following three qualities are known :—" Prime Crude," " Brown Strained," and " Light Strained Oil." Frequently the oils are differentiated into four grades : A, B, C, and D. A being extra pale, B pale, C brown, and D dark brown oil. Since the menhaden oil industry extends now along the Atlantic coast even down·to Texas, the trade differentiates also between northern menhaden oil and southern menhaden [2] oil. It is therefore desirable that in future the origin of an oil, the characteristic numbers of which are published, be described as fully as possible. The process of refining consists mainly in brightening the oil by filtering, etc.

The light-coloured oils are allowed to rest some time in the cold whereby " stearine " separates ; thus the " winter oils " are obtained. They are then bleached by filtering over fuller's-earth, etc. ; in this manner two grades are obtained, viz. " bleached winter white " and " bleached winter " oils.

Menhaden oil consists almost entirely of glycerides, as is shown

[1] Cp. J. Turrentine, Journ. Ind. Eng. Chem., 1913, 378.

[2] Southern Menhaden oil, " A " quality, is very pale but contains more " stearine " than the northern oil ; as the trade term runs, it is more " tender " and congeals readily at low temperatures.

by its saponification value, the proportion of glycerol it yields on saponification, and the small amount of "unsaponifiable matter." The chemical composition of the unsaturated glycerides is not known yet. *Bull* states that he isolated from a specimen of menhaden oil 23 per cent of a fatty acid, having the neutralisation value 197·0, and absorbing 312·5 per cent of iodine.

As clupanodonic acid absorbs theoretically 367·7 per cent of iodine, the acid isolated by *Bull* must have contained considerable quantities of clupanodonic acid.

Two specimens of hardened marine animal oils examined by *Grimme* [1] had a tallowy consistence, and gave the following characteristics :—

Specific gravity at 15° C.	0·9271	0·9256
Melting point, ° C.	47·2	38·5
Solidifying point .	34·9	31·5
Refractive index at 40° C.	1·4529	1·4575
Acid value	1·94	· 1·00
Saponification value	189·3	188·8
Iodine value (Wijs)	23·24	58·34

Grimme states that the colour reactions of hardened fish oils do not correspond with those of the raw oils. He also gives a table of colour reactions of hardened seal, whale, liver and fish oils, without, however, indicating to what extent hydrogenation has been carried out.

The amount of unsaponifiable matter found by several observers is given in the following table :—

Unsaponifiable Matter

Colour of the Oil	Per cent.	Observer.
Pale yellow .	0·61	Fahrion
Red . . .	0·82	,,
Yellowish-red (Levantine) .	1·43	,,
Brown	1·60	Thomson and Ballantyne
Extra pale . . .	1·43	Bull

The unsaponifiable matter consists chiefly of cholesterol, to the presence of which the slight optical activity of menhaden oil is due. A sample examined by *Liverseege* showed in a 200-mm. tube a deviation of − 1°; the same sample gave in the *Valenta* test 80° C.

Jean found in menhaden oil 0·02 per cent of iodine.

[1] *Chem. Revue*, 1913, 129.

[TABL_

Physical and Chemical Characteristics of Menhaden Oil

Specific Gravity		Solidifying Point		Saponification Value		Reichert Value	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	c.c. 1/10 norm. KOH.	Observer.
15	Bull	−4	Jean	188·7	Bull		
,,	Thomson and Ballantyne			189·3	Thomson and Ballantyne		
15/15·5[2]	A. Lusskin[1]			193[4]	Bull	1·1[5]	Lewkowitsch
	Lewkowitsch						
	,,						
	,,						

Specific gravity values: 0·9311, 0·9311, 0·9284, 0·9272[3], 0·9259[2], 0·9359[6]

Physical and Chemical Characteristics of Menhaden Oil—continued

Iodine Value		Maumene Test		Butyro-refractometer		
Per cent.	Observer.	°C.	Observer.	°C.	"Degrees."	Observer.
147·9	Archbutt	123–128	Archbutt	25	80·7	Liverseege[7]
160	Thomson and Ballantyne			40	71·3[8]	Lewkowitsch
153·9	Schweitzer and Lungwitz	Specific Temp. Reaction.		40	72[8]	,,
172·6	Bull					
139·2[4]						
165·7	A. Lusskin[1]	306	Thomson and Ballantyne			
150·4[3]	Lewkowitsch					
192·9[2][9]	,,					
180·0[6]	,,					

[1] Regular market quality, 1911–1912.
[4] "Natural pressed" menhaden oil.
[7] *Analyst*, 1904, 211. The optical rotation of the sample examined was −1·0° in a 200-mm. tube, the Valenta test 89° C.
[8] Northern Menhaden oil.

[2] Strongly acid oil.
[5] Neutralised oil.
[9] This oil yielded about 40 per cent of insoluble bromides.

[3] Bleached winter oil.
[6] Neutral oil.

For the detection of menhaden oil in cod liver oil, *A. Hoppenstedt*[1] gives the following colour reaction :—5 c.c. of the oil are placed in a test-tube together with 5 c.c. of acetone. 1 c.c. of concentrated hydrochloric acid is added and the tube shaken for one minute. The contents are then mixed with 5 c.c. of petroleum ether and allowed to separate. In the case of pure menhaden oil the lower layer assumes an intense bluish-green colour, whereas the cod liver oil gives a yellow to brown colour. In a mixture of equal parts of cod liver oil and menhaden oil the green colour predominates, but a mixture containing 20 per cent of menhaden oil can no longer be recognised as the green colour is masked by the brown colour of the cod liver oil.

Alsop[2] believes that menhaden oil can be detected in cod-liver oil by the acid, saponification, and iodine values, and specific gravity. He gives the following summary of some analyses of cod oils and menhaden oils :—

	Cod Oils.				Menhaden Oils.		
	Mini-mum.	Maxi-mum.	Average.	Brown Oils.	Mini-mum.	Maxi-mum.	Average.
Specific gravity	0·922	0·9270	0·9245	0·9235-0·9255	0·928	0·9349	0·920-0·931
Acid value	11·9	39·4	24·8	..	3·53	11·74	5-8
Saponification value	180	195	184-190	..	189·6	198	190-195
Iodine value (Hubl)	132	160	135-145	..	145	170	150-160

Menhaden oil is frequently adulterated with mineral and rosin oils.

Its principal use is in the currying trade, and in the manufacture of sod oil. The oil is also employed in soap-making, for the tempering of steel, and for adulterating Newfoundland cod liver oil and paint oils,[3] and also in the manufacture of linoleum. It is also used for a rubber[4] substitute and for making waterproofing solutions.[4] The oil used for paint-making should be a " winter oil " containing very little solid glycerides and also the least possible amount of free fatty acids. Cobalt tungate is stated by *Lusskin*[5] to yield the best results when used as a dryer. When linseed oil is high in price, menhaden is used to a considerable extent as a substitute for linseed to the detriment of the quality of the products.

[1] *Journ. Amer. Leather Chem. Assoc.*, December 1910.

[2] *Ibid.*, 1910, 204.

[3] E. W. Mann, *Journ. Soc. Chem. Ind.*, 1903, 1357, describes a menhaden oil containing 6·73 per cent of unsaponifiable matter, and having the Reichert value 2·2 and the iodine value 145·8. These abnormal numbers have not been embodied in the tables.

[4] English patent 26,789, 1910.

[5] *Eighth Int. Cong. Appl. Chem.*, 1912, sect. v. e (12), 156.

JAPANESE SARDINE OIL, JAPANESE FISH OIL

French—*Huile de sardine du Japon.*   German—*Japanisches Fischol.*
Italian—Olio di sardine del Giappone.

For table of characteristics see p. 417.

Japanese sardine oil is obtained from *Clupanodon melanosticta,*
T. and S. (Japanese : *ma-iwashi*), a fish belonging to the *Clupeidæ.*
The fish is chopped and boiled with water, the oil then separates on
the top.   When there is a scarcity of labour—as happens during the ·
fishing seasons—the fish is allowed to rot in heaps ; the greater part
of the oil then flows out and the remainder is subsequently recovered
by pressure.   The oil obtained by the first process is limpid and can
be easily refined, whereas the oil from the second process has a very
dark colour and a nauseous taste.   The crude oil contains about 30
per cent of " stearine." [1]   It is refined in Yesso and Yokohama by
heating to 50°-60° C. for an hour, and then running it off into wooden
vessels, where it separates into three layers.   The upper layer is liquid
and clear, the middle layer consists of solid fat,[1] and the lowest layer of
water intermixed with albuminous substances and " scrap."

Owing to the extension of railway facilities the fish is now largely
sold for food.

By far the greater part of sardine oil produced in Japan is exported
to Europe.   In 1905, 14,130 tons (2,379,267 kin, valued at 125,260 yen)
were shipped abroad.   The remainder is used at home for tanning
leather, preparing paints, etc.

As the commercial Japanese sardine oils sold hitherto were more
or less mixed with other fish oils, the numbers placed against " Com-
, mercial Oils " in the table of characteristics, p. 417, refer to oils the
genuineness of which cannot be vouched for.   The same strictures
apply to the numbers given in the following table, due to *Fahrion* :—

	I	II	III	IV	V.	VI	VII	VIII.
	Iodine Value.	Acid Value.	In-soluble Acids + Un-saponi-fiable	Oxidised Acids Per cent	Un-saponi-fiable Per cent.	Fatty Acids freed from Oxidised Acids Per cent	Molecular Weight of VI.	Neutralisa-tion Value of the Fatty Acids freed from Oxi-dised Acids.[2]
Japanese fish oil, pale . .	164 0	10 8	95 52	1 16	0 62	93 84	282 8	185·8
„ brown	157 6	34·2	96·58	0 75	0 67	95 16	281·7	189·1
„ pale	135 7	12 3	97·04	0 41	0·82	95·81	295 7	181·4
„ reddish-brown	108 5	34·5	96·82	0 62	0 86	95·34	296 6	·180·0
„ yellow .	100·1	28 2	96 51	0·49	0 79	95 23	290 2	188·8

[1] This solid fat, brought into commerce under the name "refined fish tallow," is
chiefly used as a dégras substitute for currying leather (*Journ. Soc. Chem. Ind.,*
1894, 894)   Cp. also Vol. III. Chap. XVI.
[2] This number is termed by *Fahrion* "Inner saponification value."

Physical and Chemical Characteristics of Japanese Sardine Oil

	Specific Gravity			Melting Point		Saponification Value		Iodine Value		Refractive Index		
	At °C		Observer.	°C.	Observer.	Mgrms KOH	Observer.	Per cent.	Observer.			Tsujimoto
										20° C	1·4802-1·4808	
										Butyro-refractometer.		
										"Degrees"		Observer.
										°C.		
Commercial Oil	15	0·916	Fahrion	20-22	Villon	189·8-192·1	Lewkowitsch	121·5	Lewkowitsch	40	56	Lewkowitsch
	,,	0·9272-0·9338	Bull					134·1-171·3	Bull	40	61	,,
Oil from *Clupanodon melanosticta*	15·5	0·9316-0·9347	Tsujimoto			194·8-196·2	Tsujimoto	180·6-187·3	Tsujimoto			

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Fatty Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Ether-insoluble Bromides.	
			Titer Test.		Capillary Tube.			
	Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
Commercial Oil	94·5-95·3	Fahrion	28·2	Lewkowitsch	...		...	
Oil from *Clupanodon melanosticta*	...		...		35·4-36·2	Tsujimoto	44·2-47·1	Tsujimoto

The following notes also refer to " Commercial Oil " :—

A sample of Japanese fish oil examined in the author's laboratory by *Walker and Warburton* [1] yielded 21·22 per cent of ether-insoluble brominated glycerides ; the mixed fatty acids gave 23-23·3 per cent of an ether-insoluble bromide which became black at 200° C., without melting. Another sample of Japanese fish oil containing some liver oil, and deodorised on a large scale by a special process, yielded, in the bromide test, 49-53·3 per cent of brominated glycerides ; its mixed fatty acids gave 38-39·3 per cent of a brominated product which turned black at 200° C., without melting.

Bull states that he has isolated from a number of Japanese fish oils 5·75-26·4 per cent of liquid fatty acids, absorbing 292·8-358·3 per cent of iodine.

Three specimens of undoubtedly pure Japanese sardine oils, free from other fish oils, were examined by *M. Tsujimoto*.[2] The characteristics obtained by him are recorded in the table, p. 417. On brominating the mixed fatty acids 47·09, 44·24, and 44·88 per cent respectively of clupanodonic octobromide were obtained. Since 100 parts of the octobromide correspond to 30·16 parts of clupanodonic acid, the mixed fatty acids of Japanese sardine oil contain 13·34-14·20 per cent of clupanodonic acid.

Clupanodonic acid and other acids of the series $C_nH_{2n-8}O_2$ can be partially removed by distilling the fatty acids in a current of superheated steam or under reduced pressure, as these acids do not distil so readily as the less unsaturated acids [3]

Japanese fish oil must not be confounded with Japanese cod liver oil. Japanese fish oil is used in Europe in the leather industries, and for making soft soap.

SARDINE OIL

French— *Huile de sardine.*   German—*Sardinenöl.*
Italian—*Olio di sardine.*

This oil is obtained from *Clupea sardinus*, L., in the preparation of tinned sardines. The heads of the sardines are cut off, and the oil is expressed from the " scrap." Large quantities of this oil are prepared on the Spanish and French coasts. The oil recovered on the Spanish coast has been exported chiefly to Germany, ostensibly to be used in the manufacture of varnishes (see below).

Some characteristics of sardine oils, due to *Fahrion*, are given in the following table :—

[1] *Analyst*, 1902, 237.
[2] *Journ. Coll. Eng. Tokyo Imp. Univ.*, 1906, vol. iv. p. 1.
[3] Tsujimoto, *Chem. Revue*, 1913, 8.

	I. Iodine Value.	II. Acid Value.	III. Insoluble Acids +Unsaponifiable.	IV Oxidised Acids. Per cent	V. Unsaponifiable Per cent.	VI. Fatty Acids freed from Oxidised Acids Per cent	VII. Molecular Weight of VI.	VIII. Neutralisation Value of the Fatty Acids freed from Oxidised Acids.[1]
Sardine oil, yellow . .	191·7	19·2	95·60	0·61	0·48	94·51	285·7	185·2
,, red . . .	167·0	24·7	96·55	1·35	1·01	94·19	297·7	177·2
,, reddish yellow	166·9	4·6	97·08	0·94	0·63	95·51	299·5	179·5

The solid fatty acids in a specimen of sardine oil examined by *Fahrion* were at first stated to consist of palmitic acid only ; afterwards he modified this statement by allowing a small quantity of stearic acid, palmitic, however, preponderating. The liquid fatty acids did not contain physetoleic acid (Chap. III.), nor could oleic, linolic, or either of the two linolenic acids be detected. The unsaturated fatty acid was stated to be *jecoric acid*, $C_{18}H_{30}O_2$ (from *jecur*, liver ; though sardine oil is not a liver oil), an isomeride of linolenic acid, but differing from it essentially in that it does not conform to *Hazura's* rule (Chap. III.). According to this rule it should yield, on oxidation with potassium permanganate in alkaline solution, a hexahydroxy acid, whereas it is apparently broken down with the formation of carbonic and volatile fatty acids. *Fahrion* considered this specimen of sardine oil to consist of 14·3 per cent of tripalmitin, and of 85·7 per cent of trijecorin.

These results have been severely criticised by *Weiss*,[2] and stand greatly in need of confirmation.

It has already been pointed out above that *Tsujimoto* could not detect any jecoric acid in Japanese sardine oil, and it may therefore be taken that neither does European sardine oil contain this acid. It seems most likely that also the European sardine oil contains clupanodonic acid This could be readily proved by examining the behaviour of the brominated acids in the melting point test.

Sardine oil is put to the same uses as Japanese sardine oil. The employment of the oil in the varnish industry can only be looked upon as an experiment which, doubtless, has led to failure.

The oil from *Clupea longiceps*, described by Hooper,[3] has been proposed as a substitute for whale oil in jute " batching."

SALMON OIL

French —*Huile de saumon*.   German—*Lachsöl*.
Italian—*Olio di salmone*.

This oil is obtained on a very large scale from the salmon (*Salmo salar*, L.) as a by-product in the salmon-preserving industry of British

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[1] This number is termed by Fahrion, " Inner saponification value."

[2] *Journ. Soc. Chem. Ind.*, 1893, 937.

[3] *Ann. Rep. Indian Museum, Ind. Sect.*, 1910/11, 6.

Columbia. The fish contains about 20 per cent of oil. The oil is pale golden yellow, has a mild smell, and a tolerably pleasant taste.

The sample examined in the author's laboratory by *de Greiff* [1] gave the numbers recorded in the following table of characteristics :—

Physical and Chemical Characteristics of Salmon Oil

Specific Gravity at 15·5° C	Saponification Value	Iodine Value	Reichert-Meissl Value.	Refractive Index, Butyro-refractometer.	
				°C	"Degrees."
0 92586	182 8	161 42	0 55	25	78
				40	69 5

				Per cent
Insoluble acids + Unsaponifiable .	.	.	.	95·02
Iodine value of the liquid fatty acids	.	.	197 4

The oil is imported in large quantities into this country, and is used in the leather and soap industries.

HERRING OIL

French—*Huile de hareng.* German—*Heringsol, Heringstran.* Italian—*Olio di aringhe.*

For table of characteristics see p. 122.

This oil is obtained from the several species of herring, *Clupea harengus* (North Sea), *C. pallasi*, C. and V. (Japan). Undoubtedly genuine samples of herring oil extracted from fish caught in Hokkaido, and prepared on a large scale in the same fashion as Japanese sardine oil (p. 416), were examined by *Tsujimoto*.[2] On standing, the Japanese herring oils deposited some "stearine."

The exports of herring oil from Norway are given in the following table :—

	Hkl.	Kronen
1907	1,247	26,700
1908	8,063	127,500
1909	16,561	298,100
1910	20,038	501,000

The bulk of the oil is exported to Germany, Austria-Hungary, Great

[1] *Chem Revue*, 1903, 223.
[2] Tsujimoto, *Journ. Coll. Eng. Tokyo Imp. Univ.* vol. iv, No. i., 1906.

Britain, France, Belgium, and Holland. The scrap is worked·up for manure.

The Japanese herring oils yielded on brominating 3·82 per cent and 6·54 per cent respectively of clupanodonic octobromide (see above). The unsaponifiable matter in the samples examined by *Bull* varied from 1·3 to 10·7 per cent, and the acid values from 1·8 to 10·2, whereas the Japanese herring oils examined by *Tsujimoto* had the acid values 2·02-10·42, and yielded from 0·87 to 1·4 per cent of unsaponifiable matter.

Herring oil, like all other fish oils, is largely used in the leather industry. *Procter and Holmes* [1] have ascertained the changes which fresh herring oil and " herring refuse oil " undergo on blowing with air for the number of hours stated in the table, at about 100° C.

Fresh Herring Oil

Blown	Specific Gravity.	Refractive Index	Iodine Value
0 [2]	0 923	1 4780	145 0
3	0 923	1 4781	145 0
6	0·923	1·4781	141·0
9	0·926	1 4790	135 0
12	0 927	1·4795	133 0
15	0 930	1·4800	132·0
18	0 932	1 4805	130 0

Herring Refuse Oil

Blown	Specific Gravity	Refractive Index	Iodine Value
0 [2]	0·923	1 4784	116 0
3	0·923	1·4784	113 0
6	0 924	1 4785	112 0
9	0 925	1 4786	111 0
12	0 926	1·4790	138 0
15	0·927	1·4795	136·0
18	0·928	1 4795	132 0

A. Lusskin [3] states that the drying property of the oil, even after boiling with dryers, is inferior to that of menhaden oil. The following characteristics are given for four herring oils :—

	Herring Oil. No 1.	Herring Oil. No 2	Herring Oil. No 2. Blown.	Herring Oil. No. 2. Winter-pressed. Refined.
Specific gravity at 15° C.	0 9240	0·9210	0 9654	0·920
Acid value	2·4	41 9	25 7	39·4
Iodine value	137 9	136 1	89 94	136·1
Colour	Very pale	Dark brown	Deep red	Extremely pale
Odour	Good	Bad	Almost none	Fair

[1] *Journ. Soc. Chem. Ind.*, 1905, 1287.   [2] Original oil.
[3] *Eighth International Congr. Appl. Chem.*, 1912, xii. 155.

Physical and Chemical Characteristics of Herring Oil

	Specific Gravity.			Saponification Value			Iodine Value.	
	°C		Observer	Observer.	Mgms KOH	Observer.	Per cent	Observer
Clupea harengus	15	0.9202-0.9391	Bull[1]	Bull	179-193.7	Bull	131.0-142	Bull
							123.5	Fahrion
Clupea pallasi, C and V.	15.5 / 15	0.9178-0.9251 / 0.9210	Tsujimoto / Lissmann[2]	Tsujimoto	185.9-190.5	Tsujimoto	109.1-123.4 / 1 to 1	Tsujimoto / Lissmann

[1] Seven samples containing 10-13.3 per cent of liquid acids having iodine values from 289.3 to 319.8.
[2] The acid value is 41.9.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Acids +Unsaponifiable		Melting Point		Mean Molecular Weight		Oxidised Acids		Ether-insoluble Bromides	
	Per cent	Observer.	°C	Observer	Mgms KOH	Observer.	Per cent	Observer.	Per cent	Observer.
Clupea harengus	95.64	Fahrion			291.9	Fahrion	1.59	Fahrion	...	...
Clupea pallasi.			30-31.5	Tsujimoto	...	...	...	...	12.7-21.7	Tsujimoto

Oil.	German.	French.		Oxidised Acids. Per cent.	Insoluble Acids + Unsaponifiable Per cent.
Bonito oil (1)				0·63	
Bonito oil (2)				0 49	
Tunny fish oil				0 62	
Mackerel oil					
Stickleback	Stichlingstran	Huile de trois-épines	Olio	0·62	95 78
Akaïei oil					
Anchovy	Anchovistran	Huile d'anchois	Oho		
Pilcher (Sardel)	Sardellenöl	Huile de pilchard	Olio		
Mackerel pike				0·26	
Saith oil, coal fish, pollock					94 0
Whiting	Weissfischöl	Huile de cyprin	Olio		
Sprat	Sprottenol (Sprottentran)	Huile d'esprot, melet harenguet	Oho gre		95 1
Sturgeon	Störtran	Huile d'esturgeon	Oho		
Hoi [4]	Hoiöl	Huile de hoi			
Hoi					
Eel oil					
Cramp fish	Zitterrochenöl	Huile de torpille [6]	Olio		
Sun fish [1]	Mondfischol	Huile de mole de Méditerranée	Oho me		
Carp	Karpfenol	Huile de carpe	Oho		

[1] With regard to the liver oils see table facing p. 447
[2] Zeits. f. Unters. d. Nahrgs- u. Genussm., 1906, xii. 341.

[4] Norwegian name, me
Squalida, called "hoe" i
[5] Analyst, 1904, 21
test, 113° C. Refraction

DAB OIL

French—*Huile de limande.*

This oil is prepared on the north-east coast of Houshiu (coasts of Aomori, Iwate, Miyagi) from a fish (Japanese name " Karei ") which is probably a species of *Limanda.* The oil is reddish yellow in colour and deposits stearin on standing in the cold. The following characteristics were determined :

Oil—

Specific gravity at 15° C.	0·9240
Saponification value	185·32
Iodine value (Wijs)	118·53
Acid value	0·83
Refractive index at 20° C	1·4748

Fatty Acids—

Melting point, ° C.	29
Ether-insoluble brominated acids, per cent	18·66
Oxidised acids, per cent	0·72

From the percentage of insoluble bromides *Tsujimoto* [1] calculates the mixed fatty acids to contain 5·63 per cent of clupanodonic acid.

Lesser known fish oils, see table opposite.

β. Liver Oils

The liver oils contain notable amounts of cholesterol and other unsaponifiable substances. These bodies must be looked upon as the chromogenetic substances producing the colour reactions (especially when the oils are rancid) which were formerly considered as characteristic of liver oils. At present only the sulphuric acid colour test can be looked upon as having decisive importance ; the blue colouration which *fresh* liver oils in a solution of carbon bisulphide give with conc. sulphuric acid is very distinct ; if the oils are rancid a purple, or even dark brown, colouration takes the place of the blue. Experiments carried out in my laboratory on a number of liver oils obtained from different fish, as also experiments by *Tichomirow and Kaiser,* [2] confirm that this colour test is a general reaction for liver oils. The observation made by the author (Chap. VII.), viz. that some blubber oils also give the blue colouration in the sulphuric acid test, was explained by assuming an admixture with liver oil. *Thomson and Dunlop* have, however, recently stated that a seal oil of undoubted purity, as also a genuine porpoise oil, showed the blue violet colouration with concentrated sulphuric acid.

[1] *Journ. Coll. Eng. Tokyo Imp. Univ.,* 1908, vol. iv. 177.
[2] *Chem. Zeit. Rep.,* 1895, 310.

The *intensity* of the phospho-molybdic acid test (Chap. VII.) is also characteristic. If the chloroformic solution of a liver oil, after shaking with the phospho-molybdic acid reagent, be allowed to stand, there is formed a blue ring at the zone of contact of the two layers, no doubt due to the neutralising action of the bases in the oil. In this form the phospho-molybdic test may serve to identify a liver oil. Rancid liver oils, however, do not give a distinct colour reaction. Whereas the sulphuric acid test, as a rule, indicates liver oil, the phospho-molybdic acid test must not be looked upon as having the same import-ance for discriminative purposes.

<div align="center">COD LIVER OIL</div>

French—*Huile de foie de morue.*   German—*Dorschleberol, Leberol.*[1]
Italian- -*Olio di fegato di merluzzo.*

For tables of characteristics see pp. 433, 434.

Genuine cod liver oil is obtained from the liver of the cod, *Gadus morrhua* (and of the dorsch, the young of *G. morrhua*, formerly con-sidered a separate species, *Gadus callarias*).

The habitat of the cod is not yet known precisely, yet annually at certain times enormous shoals of cod frequent the coast of the northern seas, chiefly the coasts of Norway, Scotland (Iceland), the east coasts of the United States and of Canada, the coast of Newfound-land, as also the west coast of the United States and the coasts of Japan and Siberia. The best known and oldest fishing-grounds are those of Norway, where the fish makes its appearance at regular seasons. Thus in the Lofotes the cod appears in February, and the fishing season lasts from February till April. Then the cod makes its appearance at Finmarken in June, but here the fish seem to arrive in a still immature condition, and hence do not yield as much oil as the fish caught off the Lofoten coast. Moreover, the cod frequenting the Finmarken coast is accompanied by other fish, whose livers naturally become mixed with those of the cod. Hence the Finmarken cod liver oil is not considered of the same high quality as the Lofoten oil. The chief object of the cod-fishing industry was, of course, to " cure " the fish after cleaning it, the livers being thrown away together with the most putrescible parts of the fish, which did not permit of curing. No doubt the manufacture of cod liver oil was due to the accidental discovery that from the heaped-up livers an oil exuded, which was found to possess medicinal properties. Since then the cod liver oil industry has assumed considerable dimensions, as may be gathered from the fact that in 1905, 41,907 hectolitres of medicinal oil (and 12,960 hectolitres of cod oil), and in 1906, 42,908 hl. of steam cod liver oil, were produced in Norway.

The following table shows the variations in the production of cod

[1] The German term " Kabeljauleberol " should not be applied to cod liver oil, but should be reserved for haddock liver oil (see table facing p. 447).

liver oil in the Lofoten Islands during the last twenty-three years.[1]
The numbers given for March and April include the production of the
previous months :—

Production of Medicinal Cod Liver Oil in the Lofoten Islands

Year	January-February	March	April	Equivalent in Barrels
	Hect.	Hect.	Hect.	
1886	2990	9,329	10,000	8,620
1887	753	8,041	9,500	8,169
1888	3442	15,057	16,100	13,879
1889	655	7,933	12,900	11,120
1890	2261	14,340	16,700	14,396
1891	420	13,570	19,600	16,896
1892	1970	6,600	7,920	6,828
1893	3178	15,528	18,550	15,992
1894	1993	8,160	12,231	10,544
1895	845	10,700	12,300	10,604
1896	400	6,210	8,850	7,629
1897	2336	11,000	18,260	15,711
1898	600	6,510	11,254	9,702
1899	1934	11,299	18,450	15,906
1900	1301	7,965	10,752	9,269
1901	1592	12,051	15,889	13,697
1902	631	7,768	9,628	8,300
1903		252	614	529
1904		833	2,690	2,319
1905	374	6,183	11,193	9,909
1906	3232	12,971	16,952	14,614
1908				51,000
1909				43,000

In Newfoundland and on the coast of Labrador the cured fish was
also the main product, and the liver oil industry has only gradually
assumed the proportions it possesses to-day. The chief attention
having been paid to the fish, the cod liver oil industry has lagged
behind that of Norway as regards medicinal cod liver oil, although the
nearness of the fishing-grounds to the rendering establishments per-
mitted, at an early stage of the cod oil industry, the production of
commercial *cod oil* of a better quality than could be obtained in this
country (see below). During the last few years the cod fish industry
has assumed enormous dimensions on the Pacific coast, especially so
of the United States, and bids fair to surpass in dimensions the great
industry of the east coast of America. Up to a few years ago San
Francisco was the greatest cod fish centre of the Pacific coast, the fishing
vessels, which exploited chiefly the fishing-grounds near the Shumagin
Island on the south of Alaska, bringing their cargoes to San Francisco.
Recently enormous rendering establishments have been erected at
Anacortes in Puget Sound, and also at Vancouver. (In British Columbia
hitherto little attention has been paid to the cod industry, as the chief

[1] Bousfield, *Chemist and Druggist*, 1907, 207.

interest was centred in the catch of salmon and halibut.) All estab-
lishments in the three curing stations named send out fishing flotillas
to the south of Alaska. At present the manufacture of medicinal cod
liver oil plays an unimportant part on the west coast of America, as the
amount of detailed attention required in the production of the best
qualities is still wanting.

Latterly Japan has also entered the lists as a manufacturer of cod
liver oil, both medicinal and commercial. The enormous fishing-
grounds in the Okhotsk sea, where cod is most plentiful, have been
leased to the Japanese, and a large production of both medicinal oil,
as also commercial cod oil, may be expected in the near future.

In order to illustrate by a few figures the extent of the cod industry,
and indirectly that of the cod liver oil industry, it may be stated that
the marketed value of the cod products of Canada were estimated at
3,368,750 dollars in 1912. The exports from Newfoundland in 1912
were 9,418,000 kilos. of fish.

The fish is caught either by hook and line or in nets (cod traps).
The latter method is extensively used where the fish can be driven into
narrow fjords, as e g. in Norway. It is said that the fish caught in net
is fatter, and yields therefore a larger liver and more oil, than the fish
caught by hook and line. The head of the fish is severed from the body,
the fish split along the abdomen, and the liver thrown out by the
operator by a rapid jerk.

In the early years of the manufacture of cod liver oil the livers were
heaped up in barrels and allowed to undergo a process of spontaneous
putrefaction, whereby the liver cells burst and the oil exuded. The oil
so obtained was contaminated with decomposition products of the liver,
and therefore possessed a rank odour and nauseous taste, with which
even nowadays popular prejudice associates medicinal cod liver oil.
With the increased facilities of intercourse between the cod-fishing
stations and properly equipped rendering establishments, this exceed-
ingly crude process of manufacture underwent considerable improve-
ments. The livers were then properly sorted and washed as rapidly as
possible, so as to inhibit the spontaneous decay which sets in on exposure
of the livers to the air. Moreover, the oil exuding from the livers was
collected in fractions as it were, and thus graded, the oil running out at
first, as the best, being kept separate from the oils obtained from the
livers in a more advanced state of decomposition.

Thus up to a few years ago the following three qualities of cod liver
oil, as obtained by the natural decay of the livers (in the Lofoten
Islands), were known in commerce : (1) pale cod liver oil, (2) light
brown oil, (3) brown oil.

Pale cod liver oil [1] and *light brown oil* are used in pharmacy. The
former is the first product, the light brown oil forming the second
product, after the disintegration of the livers has proceeded further.

The *brown oil* was that obtained from the livers which had reached
a very advanced state of decay, and had actually become putrid. This

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[1] The pale yellow colour is due, according to P. Moeller, to a pigment (lipochrome)
which is destroyed by the action of bright light ("sun-bleached oils").

oil was recovered by boiling the putrid livers with water, skimming off the oil, and finally pressing the scrap (see below).

Even the following four qualities of cod liver oil, which were differentiated by *P. Moeller*,[1] viz. (1) *raw medicinal*, (2) *pale oil*, (3) *light brown oil*, (4) *brown oil*, are no longer recognised in the trade. Besides, so little was obtained of the raw medicinal oil, that it did not pay to collect it separately.

During latter years the manufacturing processes of cod liver oil, especially those of medicinal oil, have undergone a complete change, chiefly in consequence of the erection of properly equipped establishments in the Lofotes by English pharmacists. The demand for pure medicinal cod liver oil had already forced some pharmacists in this country to prepare the medicinal oil themselves, by heating absolutely fresh livers, taken from fish brought to shore alive, in jacketed vessels heated by hot water or by steam. Under the action of the high temperature the cell membranes burst, and the oil exuded. The best medicinal oil—termed " steam liver oil "—was thus obtained. This method was taken up by cod oil extractors in Hull, Aberdeen, Dundee, etc., and finally transferred to the above-mentioned rendering establishments in the Lofotes. The best medicinal oil is manufactured there on the lines sketched for the manufacture of " steam liver oil." The livers are worked up immediately after being taken from the fish so as to avoid exposure to the air, it having been found an invariable experience that even exposure for a few hours was apt to cause deterioration in the quality of the oil. This process, taken as it were from the laboratory, was found too cumbersome and too slow, since the extraction of the oil from the livers required several hours. At present, in the best equipped establishments in Norway, the fresh livers are placed in tin-lined vessels, provided with open steam coils, almost immediately after they have been taken from the fish, washed, and sorted – all livers showing stains being discarded. Low pressure steam is then blown into the livers, and the oil exudes almost immediately.[2]

The best qualities of crude medicinal oil are prepared in this manner. Previously, the Norwegian medicinal oil was looked upon as the best brand in the market, no doubt owing to the fact that in former years the nearness of the fishing stations to the rendering establishment and the careful sorting of the livers secured the best oil that could be produced under the then ruling circumstances. Although the conditions favouring the immediate working up of the livers also prevail in Newfoundland, the details of the manufacturing operations were formerly not carried out with sufficient care to secure an equally good oil. Hence the Newfoundland oil was considered as much inferior to the best Norwegian medicinal oil. At present, however, the most modern methods of manufacture have been introduced also into Newfoundland. Since the Newfoundland manufacturers have adopted the packages used by the Norwegian makers and abandoned wood, which was always

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[1] Moeller, *Cod Liver Oil and Chemistry*, London, 1895, where complete details as to the old processes of manufacturing cod liver oils in Norway are given.

[2] Michaelis and Pechstein, *Biochem. Zeits.*, 1913 (53), 320.

apt to impart an undesirable flavour to the oil, Newfoundland medicinal cod liver oil can no longer be considered as inferior to Norwegian oil. It is to be expected that the demand for oil of unobjectionable taste will entirely do away with antiquated methods, and that the manufacture of " pale cod liver oil " and " light brown oil," obtained from naturally *decayed* livers, will die out completely.

The medicinal oils in the market, prepared by the processes sketched above, are of such excellence that it would hardly appear necessary to have recourse to more elaborate details, such as the extraction of the oil in a vacuum pan,[1] or in a current of carbon dioxide.

The crude medicinal cod liver oil is filtered to free it from liver tissue, and bleached by treatment with fuller's earth, or by exposure, in closed glass vessels, to the action of sunlight. Medicinal oil so prepared deposits " stearine " at a low temperature, and such oil is termed " congealing oil." Some Pharmacopœias, such as the British Pharmacopœia, prescribe a " non-congealing " oil, *i.e.* an oil which will not set at the freezing point. Such medicinal oil is obtained by allowing the crude medicinal oil to cool down to below $0°$ C., and filtering it at a temperature of $-10°$ C. The " stearine " is sold as " fish stearine " of best quality, for soap-making purposes.

All unsound livers, and those which have been exposed for a shorter or longer time to the atmosphere, would then be worked up solely for " brown oil." This brown oil, if prepared exclusively from cod livers—the " cod oil " of commerce—is of course a genuine cod liver oil. Before steamers were introduced into the cod-fishing industry off the coast of Great Britain, the fishing-boats remained sometimes for a week on the fishing-grounds, and the fish could not be brought to shore alive. The livers were collected, and thus they were landed in a more or less putrid state. The gases which collected in the barrels, in consequence of the high state of putrefaction, sometimes exerted so high a pressure that the ends of the barrels—as the author has witnessed himself—were driven out. The fresher the state of the livers, the better the oil. For this reason " Newfoundland cod oil," in consequence of the nearness of the fishing station to the rendering establishment, was the best class of commercial cod oil. Next to this came the " Norwegian cod oil," which commanded a higher price than the English cod oil. The author proved on a large scale that the preference given to the Norwegian fish oil was solely due to the greater freshness of the livers from which the oil was prepared. The English oil, having undergone oxidation, required a special process of purification in order to bring it into line with the Newfoundland quality. In consequence of the displacement of sailing craft by steamers, and more recently by motor boats, the livers are now brought to shore,[2] even in this country, in a much fresher state than formerly ; hence the quality of cod oil manufactured in this country has greatly improved during the last few years.

In the manufacture of cod oil, the livers are boiled out with water,

[1] Harrison, Wild, Robb, English patent 25,683, 1904.

[2] Hence the patented appliances (Johnson, English patent 26,728, 1902) for rendering on board trawlers would appear superfluous at present.

and the oil which rises to the top is skimmed off. The scrap ("foots") is pressed in hydraulic presses to yield a further quantity of oil which is of much inferior quality. The expressed "scrap" is then worked up into "fish manure."

The crude cod oil, termed "unracked" cod oil, contains a considerable quantity of "stearine," which separates out on cooling. This "stearine" is recovered either by filtering, or by merely drawing it off from the bottom of the tanks, in which the crude cod oil has been allowed to stand for some time, exposed to cold. The "stearine" so obtained is sold for soap-making purposes, as a lower kind of "fish stearine" than that obtained from good medicinal oil, or as "fish tallow" for currying.

The commercial "Coast cod oil" is a liver oil obtained from other fish besides cod, such as hake (*Merluccius vulgaris*), haddock (*Merluccius æglefinus*), ling (*Molva vulgaris*), coal fish (*Gadus merlangus, s. carbonarius, virens*), in fact any fish that is caught in the nets of the trawlers in the open sea. The livers from these fish are collected in barrels, and usually reach the works of the cod oil extractor in a more or less putrid state, depending on the time that has elapsed since the fish has been caught.

The following table, due to *Thomson and Dunlop*,[1] shows the comparative characteristics of oils prepared by these investigators from fresh livers, for the authenticity of which they vouch :—

	Specific Gravity at 15° C	Free Fatty Acids. Per cent	Saponification Value	Un-saponifiable	Iodine Value	Butyro-refracto-meter	Reichert-Meissl Value.
Cod (West Coast) .	·9248	0 20	18 60	1 06	153 7	75 7	66 7	..
Cod (unknown) .	·9247	0 19	18 51	1 02	156 5	76·0	...	...
Cod (East Coast) .	·9263	1·20	18 79	1 04	167 3	78 0	69 0	0·4
Ling . . .	·9240	0 34	18 72	1 00	151·8	75·0	. .	.
Hake . .	·9256	1 05	19 07	1 38	154 0	76 0	.	.
Coal fish .	·9261	0 27	18 72	1 14	161·1	77 0	. .	..
Whiting .	·9290	0 65	18 79	1 06	184 2	81·0	72 0	.
Haddock .	·9290	2 37	18 72	1 30	186 4	81 0	72 0	.
Skate . .	·9298	0 33	18 79	1·08	191 1	82·5	73·5	.
Dogfish . .	·9179	Trace	16 97	8·40	126 4	71 2	62·5	...
Porpoise (blubber) .	·9352	0 10	25 66	0 67	88 3	54 8	46·3	81·4

The colour of pure medicinal oil is pale yellow or light yellow. The best qualities have only a slight fishy odour, and a not unpleasant taste. The lower qualities of cod liver oil, such as represented by cod oil, vary in colour from dark yellow down to almost black. The oil expressed from the "foots" is generally of a black colour, and has a rank, fishy odour.

According to the temperature at which the oil is recovered it contains varying quantities of "stearine." On standing at the ordinary temperature the bulk of the "stearine" settles out. Cod liver oils freed

[1] A paper read before the Association of Public Analysts of Scotland, June 1905, 5.

from "stearine" are known as non-congealing (non-freezing) or "racked" oils (cp. "Demargarinated Oils," Chap. XV.). Therefore the solidifying points of commercial samples vary considerably.

The chemical composition of the cod liver oil glycerides appears to be very complicated. Since palmitic and stearic acids have been isolated, the occurrence of palmitin and stearin must be accepted as proven. The "stearine" separating from cod liver oil on cooling contains, however, but little true "stearine," i.e. glycerides of stearic and palmitic acids. Samples of cod liver oil stearine examined in my laboratory had iodine values ranging from 94 to 102. *Heyerdahl* (evidently in a less carefully prepared specimen) found 113·4. On a large scale the author obtained from a cod oil having the iodine value 170·6 a softish "stearine" of the iodine value 116 7, whereas th liquid portion had the iodine value 178·0. By pressing the "stearine" a hard cake was obtained of the melting point 37·8° C., and of the iodine value 102·4.

Small quantities of glycerides of the lower saturated fatty acids, such as the glycerides of acetic, butyric, valeric, and capric acids, have been stated by various authors to occur in cod liver oil. The volatile fatty acids are, however, secondary products due to the putrefaction of livers, which in the older processes of manufacture always occurred to some extent. The best medicinal liver oils prepared by steam are free from volatile acids (see below).

The nature of the liquid fatty acids in cod liver oil is but imperfectly understood as yet ; their high iodine value points to the presence of larger proportions of less saturated acids than those belonging to the oleic series. *Fahrion*,[1] examining the liquid fatty acids from a cod liver oil, absorbing 175 5 per cent of iodine, could not identify jecoric acid with certainty. *Fahrion* assumes the presence of an acid, $C_{17}H_{32}O_2$, termed "asellic acid" (see Chap. III.). He could not detect physetoleic acid (iodine value = 100), stated by some writers to form the chief constituent of cod liver oil. *Heyerdahl*[2] concluded that the mixed fatty acids of cod liver oil, freed from its "stearine," contained, amongst other hitherto not identified acids, about 4 per cent of palmitic acid, 20 per cent of jecoleic acid (Chap. III.), and 20 per cent of therapic acid (Chap. III.). The presence of jecoleic acid is inferred from the existence of dihydroxyjecoleic acid (prepared by the oxidation of the mixed fatty acids with potassium permanganate), and that of therapic acid from the octobromide $C_{17}H_{26}Br_8O_2$ obtained on brominating the liquid fatty acids. No oleic acid was found in cod liver oil ; the "stearine," no doubt, contains some unknown unsaturated acid or acids. In the fresh state cod liver oil is free from hydroxylated acids.

An approximately accurate method for the resolution of the liquid cod liver oil fatty acids consists, according to *Bull*,[3] in the fractional separation of their alkali salts. Cod liver oil is saponified with double normal anhydrous alcoholic potash, and the potassium salts obtained

[1] *Journ. Soc. Chem. Ind.*, 1893, 935.

[2] *Cod Liver Oil and Chemistry*, p. lxxxix.

[3] *Chem. Zeit.*, 1899, 996.

on concentrating the solution are carefully pressed after cooling. The pressed cake is recrystallised from alcohol and pressed again, and the united mother liquors are concentrated, cooled, and pressed, these operations being repeated until a solid potassium salt is no longer obtained. The mother liquors are converted into the sodium salts by isolating the free fatty acids and neutralising them with anhydrous alcoholic soda. The sodium salts are purified in exactly the same manner as described for the potassium salts. The free fatty acids are recovered from the solid salts thus obtained, by dissolving the soaps in water in a current of steam, and gradually allowing hydrochloric acid to run on to them, until the solution is distinctly acid. From the alcoholic mother liquors the alcohol is completely removed by distilling *in vacuo.* The residue is then thoroughly exhausted with dry ether. Thus the sodium salts of the most unsaturated acids, as also cholesterol, are dissolved. The soaps are recovered from the ethereal solution by washing with water. The ether-insoluble soaps are dissolved in absolute alcohol; by allowing to crystallise, a small amount of a sodium salt may be recovered from the remaining alcoholic mother liquor. The alcohol is finally removed by evaporation and the fatty acids are liberated. Thus the following four groups of fatty acids were obtained :—

A. Fatty acids, the potassium salts of which crystallise from alcohol.
B. Fatty acids, the sodium salts of which crystallise from alcohol.
C. Fatty acids, the sodium salts of which are readily soluble in ether.
D. The remaining fatty acids.

From 1000 grms. of cod liver oil *Bull* obtained the following quantities of acids :—

Fatty Acids	Weight	Neutralisation Value	Iodine Value.
A.	334 grms.	194·2	67·5
B.	375 ,,	190	135·6
C.	120 ,,	167	322·1
D.	69 ,,	169	347

For the conclusions which *Bull* draws from his experiments, and for the analytical methods he recommends (all of which stand greatly in need of confirmation [1]), the reader must be referred to the original paper.

On brominating cod liver oil, *Hehner and Mitchell* obtained 56·23 per cent of brominated glycerides, to which they ascribed the hypothetical formula, $C_3H_5(C_{18}H_{29}O_2Br_6)(C_{18}H_{29}O_2Br_6)(C_{18}H_{33}O_2Br_2)$. *Walker and Warburton*, in the author's laboratory, found only 33·7-35·3 per cent of brominated glycerides. From a commercial cod oil, *Hehner*

[1] *Jahrbuch d. Chem.,* 1900 (v.), 386.

and Mitchell obtained 35·5 per cent of brominated glycerides, *Walker and Warburton* 30·6-32·7 per cent. The mixed fatty acids of a cod liver oil, elded to *Hehner and Mitchell* 18 per cent of a bromide containing 6.·91 per cent of bromine (theory requiring for a hexabromo compound 63·31 per cent of bromine). *Walker and Warburton*, again, obtained from a genuine cod liver oil, which gave 33·7-35·3 per cent of brominated glycerides, 29·8-30·4 per cent of brominated fatty acids. The proportion of bromo compounds no doubt depends on the state of freshness of the sample under examination. This is indeed brought out by the results of some later analyses made by *Bull and Johannesen*,[1] who obtained in ten commercial cod liver oils 27·08-34·92 per cent of ether-insoluble brommated acids. *Tolman*[2] also found the yield of insoluble bromides for a Norwegian cod liver oil 46·6 per cent, and for an American cod liver oil 34 per cent.

The foregoing notes would appear to show that fatty acids of the series $C_nH_{2n-6}O_2$ may be present in cod liver oil. An acid or acids (if any) having this composition must, however, differ from linolenic acid, since the isolated bromo compounds of the fatty acids do not melt, like linolenic hexabromide, at about 175° C., but remain apparently unchanged until a temperature of 200° C. is reached, when they are converted into a black mass, without, however, melting to a clear liquid. The difference between the unsaturated acid (or acids) of cod liver oil and the unsaturated acids of the vegetable drying oils is further exemplified by the fact that cod liver oil does not dry to a skin like the vegetable drying oils.

The following table gives a comparison of the yield of insoluble bromides from fatty acids :—

	Solid Acids	Insoluble Bromides.
	Per cent	Per cent.
Cod	5·70	46 6
Cod	15·55	34 0
Pollock	15 99	42 7
Hake	13 58	30·3
Ling	14 42	30·2
Dogfish	18 52	37·2
Trout liver	7 01	35 1
Seal	9 96	19 5

From the latest researches of *Tsujimoto* we must conclude that acids of the formula $C_nH_{2n-8}O_2$ which yield octobromides on treating with bromine occur also in cod liver oil. *Heyerdahl* appears to have been the first to prove the presence of an octobromide, but it should be pointed out that the formula of the " therapic acid " differs from that of *Tsujimoto's* clupanodonic acid, the occurrence of which has been proved so far in fish and whale oils.

[1] *Chem. Zeit.* 1909, 74. The observations were made by Dr. Pickles in the Imperial Institute.
[2] *Journ. Ind. Eng. Chem.*, 1909, 340.

Physical and Chemical Characteristics of Cod Liver Oil (chiefly medicinal oil)

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Reichert Value		Maumené Test		Refractive Index	
At °C	Observer	°C	Observer	Mgrms. KOH	Observer	Per cent	Observer	c.c. norm. KOH	Observer	°C	Observer	At °C	Observer
15	Kremel[1]	0 to -10	Salkowski	182·188	Lewko-witsch	158·7-	Thomson and Bal-lantyne	0·40-	Lewko-witsch	116	Baynes	15	1·4800-1·4852 Strohmer
,,	Bull[2]			187·1-191·4	Thomson and Bal-lantyne	166·6	Parry	0·45	Parry	100·2	Henseval and Huwart	15·5	1·4788-1·4814 Tolman[10]
,,	,, 3			173-193·4	Parry and Sage	160· 166·5	Lewko-witsch	0·76				20	1·4769-1·4800 Utz
,,	,, 4				Bull	133·11	,,					20	1·4785-1·4825 Harvey
,,	,, 6			183·188	,,	160·	Lewko-witsch						
,,	,, 6			17·165		198·1	Bull						
15·5	0·9310-0·9410 Lewko-witsch			168·3-	,,	135·							
,,	0·923-0·930 Thomson and Bal-lantyne			175·26		140·83							
20	0·9202-0·9246 Wijs[9]					159·7	Harvey[7]						
15·5	0·9259-0·9291 Parry					176·9							
15·5 (water 15·5=1)	0·9224-0·9270 Tolman[10]					154·5	Wijs						
25	, [13]					181·3	Lewko-witsch[12]						
25 (water 25=1)	0·9174-0·9220					165·9	[13]						
						169·7 170·4 163·4 172·6	Tolman[10]						

Specific Temperature Reaction   243-272   Thomson and Bal-lantyne

Oleo-refractometer.

Degrees.	Observer.	At °C.
+85 to +53	Jean	
+40 to +46	Pearmain	at 22° C.
+43·5 to +45	Dowzard[8]	at 22° C.
+40·3 to +48	Lewkowitsch[16]	

Butyro refractometer.

At °C.		Observer.
15	81·3 867	Utz
20	77·5·832	
25	75	Mänsfeld
40	71	
25	78·79·14	Lewko-witsch
40	68·5 ; 70·5	,,
25	77-80·13	,,
40	68·71	,,
25	75·15	,,
40	76	,,

1 Medicinal oil.   2 Steam liver oil, 'Lofoten.'   3 Japanese steam liver oil medicinal.   4 Pale oil   5 Light brown col.
6 Brown oil.   7 Journ. Soc. Chem. Ind. 1902, 614.   8 Pharm. Journ. Transvl. (4) 6, 582.
9 Thirty-four samples of pure cod liver oils of different qualities (Zeits. f. a. gew. Chem., 1902, 1192).   10 American cod liver oils Journ. Amer. Chem. Soc. 1906, 391.
11 Containing "stearine"   12 Newfoundland, freed from stearine.   13 Norwegian, freed from stearine.   14 Three samples   15 Not stearine free   16 Season 1907.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Kind of Oil	Solidifying Point		Melting Point of Solid Fatty Acids		Neutralisation Value		Mean Molecular Weight		Iodine Value		
Per cent	Observer		°C	Observer	°C	Observer	Mgrms. KOH	Observer		Observer	Per cent	Observer	
95·3[1]	Lewkowitsch,	Medicinal	Titer Test 17.5-18.1	Lewkowitsch	22-25	Parry	204.4	Dietench	287-290	Parry	164-171	Parry	
96·5[1]	Fahrion	Coast cod	18.7-19.3	"			207	Thorner					
		Norwegian	13.3-13.9	"									
		Dark, unpacked	22.5-24.3	"									

[1] Medicinal oil

Bull[1] examined the methylesters of cod liver oil fatty acids (cp. Chap. XII.), obtained by treating cod liver oil with sodium methylate. By subjecting the esters to fractional distillation *in vacuo* at 10 mm. pressure, three main fractions were obtained, boiling at 186° C., 206° C., and 224° C. respectively. In the following table the main results of this investigation are summarised :—

Fraction boiling from				Contains
161·5 to 165° C.	.	.	.	Myristic acid
185 „ 186° C.	.	.	.	Palmitic acid, palmitoleic acid [2]
200 „ 206° C.	.	.	.	Stearic acid, oleic acid
223 „ 225° C.	.	.	.	Gadoleic acid [3]
239 „ 240° C.	.	.	.	Erucic acid [4]

Although *Bull* distinctly mentions that acids occur in cod liver oil having very high iodine values, he appears to have overlooked those fatty acids which occur in considerable quantity in cod liver oil,[1] and yield highly brominated acids. Hence *Bull's* statement that *Heyerdahl's* jecoleic acid does not exist, and that the latter's dihydroxyjecoleic acid is possibly a eutectic mixture of dihydroxystearic acid and dihydroxygadoleic acid, must also be accepted with reserve.

The occurrence of morrhuic acid $C_9H_{13}NO_3$ (differing from tyrosine by H_2) in cod liver oil requires confirmation.

On reducing cod liver oil with hydrogen in the presence of colloidal palladium in the cold, *Paal and Roth*[5] obtained a solid fat softening at 43° C. and liquefying at 45° C. The iodine value of the reduced glyceride was 3, whereas the original oil absorbed 135·8 per cent of iodine (cp. Vol. 1. Chap. I.).

A characteristic constituent of cod liver oil is **cholesterol**. This is isolated by preparing the unsaponifiable matter in the usual manner and recrystallising it from alcohol, when the characteristic cholesterol crystals are deposited. *Salkowski*[6] gives as the average quantity of cholesterol obtainable from medicinal cod liver oils 0·3 per cent. The lævo-rotation of the plane of polarised light exercised by cod liver oil is undoubtedly due to the presence of the cholesterol. *Dunlop and Thomson* found the specific rotatory power of several cod liver oils $[\alpha]j = -0.26°$.

The somewhat considerable amount of cholesterol, which was found in the oils manufactured two or three decades ago, has led to the assumption that the slight optical activity which some high boiling mineral oils from petroleum exhibit (see Vol. III. Chap. XV.), was due to the content of cholesterol in those fish and liver oils, which are assumed to be the mother substances of the natural petroleums.[7]

Besides cholesterol, the unsaponifiable matter of cod liver oil

[1] *Berichte*, 1906, 3570
[2] Bull did not name this acid ; I suggest for it the name "palmitoleic acid."
[3] Cp. Vol. I. Chap III.
[4] Cp. Vol. 1. p 195.
[5] *Berichte*, 1908, 2283.
[6] *Zeitschr. f. analyt. Chem.* 26, 565.
[7] See Lewkowitsch, *Jahrbuch d. Chem.*, 1907 (xvii.), 417.

contains " lipochromes " to which the colour reactions, which have
formerly played so important a part in the examination and identi-
fication of cod liver oil (see below), are due. *Gautier and Mourgues*
state that they have isolated from the unsaponifiable matter a substance
similar to lecithin, inasmuch as it yielded phosphoric acid, glycerol, and
a fatty acid, termed by them morrhuic acid (see above) ; it has been
pointed out already that the existence of this acid is very doubtful.

The lecithins derived from fats contained in the animal organisms
are characterised by the facility with which they are oxidised. In
this respect they would seem to be analogous to the liver oils. It is
worthy of note that these easily oxidised substances are synthesised
in those organisms of the body which are the centre of the greatest
metabolic activity.

In the older literature on this subject there are recorded many
statements as to the occurrence of bases which were, of course, found
in the unsaponifiable matter. Undoubtedly most of these bases are
secondary products, due to the decomposition the livers underwent
whilst the oil exuded from them spontaneously. Thus, *Heyerdahl*
found in raw medicinal oil, *i e.* first oil which exuded spontaneously
from livers by natural decay, small quantities of ptomaines ; and
Gautier and Mourgues [1] before him found organic bases in " light
brown " cod liver oil to the extent of from 0·035 to 0·050 per cent.
They isolated the following bases .

(a) *Volatile* : butylamine, isoamylamine, hexylamine, dihydro-
       lutidine.
(b) *Non-volatile* : morrhuine $C_{19}H_{27}N_3$, aselline $C_{25}H_{32}N_4$.

Recently *Philip B. Hawk* [2] isolated from " light amber," " light
brown," and " dark brown " oils 0·106, 0·117, and 1·09 per cent re-
spectively of " leucomaines," by the method of *Gautier and Mourgues.*
By fractional distillation butylamine, amylamine, hexylamine, and
dihydrolutidine were separated. In the non-volatile portion mor-
rhuine was identified, but not the aselline, described by *Gautier and
Mourgues.*

Heyerdahl has isolated trimethylamine by means of its platino-
chloride. This base, however, like those mentioned above, must be
considered as a product of decomposition of the cellular tissue of the
livers. Biliary colouring matters, stated to occur by earlier observers,
are absent. According to *Salkowski* the colouring principle in cod liver
oil belongs to the class of *lipochromes.*

To most of these bases in turn have been ascribed the medicinal
properties of cod liver oil, but there seems to be no doubt that all these
bases are secondary products derived from the decayed cellular matter
of the livers. The best medicinal cod liver oils, *i.e.* those oils which
have been prepared from fresh livers by steaming, do not contain
these bases (which impart the nauseous taste to the oils obtained by

[1] *Compt. rend.*, 1888 (107), 254 ; 626 ; 740.
[2] *Proceed. Amer. Physiol. Soc.*, 1907–8, xxii. ; *Amer. Journ. of Physiol.*, 1908
(xxi.), No. 11.

the natural decay of livers). Even the amount of lipochromes and other unknown substances, such as biliary colouring matters, the presence of which is indicated by the characteristic violet colour re-action of liver oils (see p. 441 below), has decreased considerably with the improvements in the production of this oil. . Ieed, the author is of the opinion, derived from the examination of a very large number of medicinal oils of various origins, that the fainter is the blue colour reaction with concentrated sulphuric acid, the better is the taste of the oil, for the colour reaction is merely indicative of impurities which can be kept out of a properly manufactured article. It therefore follows that the statement, still occurring in the pharmaceutical literature, that a strong colour reaction indicates biliary substances (which were said to constitute the therapeutical effect of cod liver oil) is valueless. The same strictures apply to statements as to the occurrence of albu-minoid substances, some of which were credited with the power of combining chemically with iron, manganese, calcium, magnesium, and sodium.

By some writers the *therapeutic value* of cod liver oil was ascribed to the small amount of iodine it contained (therefore cod liver oils are met with to which iodine or potassium iodide has been added fraudulently). The following amounts of iodine have been recorded :—

<p align="center">*Proportion of Iodine in Cod Liver Oil*</p>

Description of Oil.	Iodine.	Observer
	Per cent.	
Pale . . .	0·020	Andrès
Yellow . . .	0·031	,,
...	0·00138-0·00134	Stanford
...	0·0002	Heyerdahl

In the opinion of the author the medicinal effect of cod liver oil, however, must rather be looked for in the facility with which it is hydrolysed or digested, and it cannot be doubted that this property is caused by the peculiar constitution of its unsaturated fatty acids. From the medicinal point of view, the best cod liver oil is that which has been prepared from fresh livers and kept protected from the action of light and air.

. Possibly the therapeutical value lies in that this oil supplies those highly unsaturated acids (clupanodonic) which have been shown to occur in the phosphatides of the heart muscles and the liver (Vol. I. p. 40), so that the explanation would be obvious, viz. that the weak organism, unable to produce for itself the unsaturated fatty acids, has them supplied artificially by the liver oil.

Heyerdahl has studied the influence which the length of time during which the livers are heated has on the proportion of free fatty acids in the oil produced. He found, contrary to expectation, that the

percentage of free fatty acids decreased slightly but perceptibly as the time of heating was increased (from 20 to 80 minutes) and the temperature was allowed to rise (from 62° to 85° C.). This result may be ascribed to the volatilisation of free volatile acids at the higher temperature, or to the fact that the first portions of the extracted oil were richer in fatty acids, or to both causes conjointly, or to the fact that enzymes causing hydrolysis (see " Lard ") were destroyed by heating. Experiments, in which measured volumes of air were driven through samples of oil heated in the water-bath, proved that the free fatty acids decreased up to a certain point, and then slowly rose to, or beyond, the original percentage. The proportions of free fatty acids never exceeded 0·69 per cent, calculated as oleic acid.

The oil obtained by passing steam directly into the livers is practically devoid of volatile fatty acids ; their occurrence in commercial oils must therefore be due to some secondary process. This statement has been corroborated by the examination of liver oils from other species of fish (*Heyerdahl*).

In the examination of *Medicinal Cod Liver Oil* the organoleptic methods must be applied in the first instance. A good medicinal oil should be of pale colour, and should have a mild fishy taste, and possess only a slight fishy odour. The taste alone is able to indicate whether the amount of free fatty acids is too high, and whether any decomposition products of the liver tissue have passed into the oil.

The *chemical* tests which furnish the most important indications for the valuation of medicinal cod liver oil comprise the *acid value*, the *iodine value*, and the *Reichert value* (*Reichert-Meissl value*).

The proportion of *free fatty acids* should be as small as possible. No definite limit can be laid down, but a comparison with the numbers recorded in the following table will afford the necessary guidance :—

Free Fatty Acids in Cod Liver Oils, calculated as Oleic Acid

Description of Oil			Colour.	Free Fatty Acids.	Observer.
				Per cent.	
Raw medicinal oil	.	.	Pale	3·79	Heyerdahl
,, ,,	.	.	Somewhat darker	3·87	,,
,, ,,	.	.	Darkest	3·96	,,
Medicinal oil	.	.	Yellow	0·36	Thomson and Ballantyne
Medicinal oils	.	.	...	0·34-0·60	Parry and Sage
,, ,,	.	.	...	0·12-0·48	Lewkowitsch
,, ,,	.	.	...	0·43-1·01	Parry

It may therefore suffice to state that the best steam cod liver oils contain from 0·3 to 1·5 per cent of free fatty acids (calculated as oleic acid), whereas medicinal oil prepared by older processes exceeds this number, and may reach as much as 3 or even more per cent.

The *Reichert value* should be low. Good medicinal oils show *Reichert* numbers lying below 0·5. A higher number, especially one exceeding 1·0, would indicate that the livers employed for the extraction of the oil have not been perfectly fresh ; such oil would also betray its high amount of volatile acids by an inferior taste.

The higher the *iodine value*, the less oxidation can have taken place, and if the medicinal properties be valued by the amount of unsaturated fatty acids, then, *cæteris paribus*, the higher the iodine value the better the oil. It will be gathered from the table of characteristics that the author found (in a cod liver oil used for feeding calves) the high number 198·1. The mean iodine value of a good medicinal non-congealing oil may be taken as 167. Since, however, the magnitude of the iodine value depends on the extent to which the " stearine " has been removed, it would not be permissible, without further examination, to declare samples having lower iodine values as adulterated.

The amount of *unsaponifiable matter* should not as a rule exceed 1·5 per cent (cp. table below). Larger amounts would point (in the absence of mineral oils) to admixture with other liver oils such as shark liver oil, which contains notable proportions of spermaceti, or of liver oil from *Merlangus* (sej liver oil, saith oil), which has been frequently substituted for cod liver oil.

Inferior cod liver oils which have a higher proportion of unsaponifiable matter should be rejected as indicating badly prepared oil. Thus Japanese cod liver oil, which has not yet been prepared according to the best methods, contains amounts of unsaponifiable matter exceeding 2 per cent.

A comparison of the amounts of unsaponifiable matter contained in best cod liver oils with those found in oils of low quality is afforded by the following table :—

Unsaponifiable Matter in Cod Liver Oils

Description of Oil.			Colour	Unsaponifiable	Observer
				Per cent	
Medicinal cod liver oil	.	.	Reddish yellow	0·54	Fahrion
,,	,,	.	Yellow	1·08	,,
,,	,,	.	Pale yellow	1·44	,,
,,	,,		Yellow	0·87	Thomson and Ballantyne
Steam cod liver oil, medicinal	.		Pale yellow	0·61	Fahrion [1]
,,	,,	,,	Almost colourless	0·64	,,
,,	,,	,,	Pale yellow	0·98	,,
,,	,,	,,	Pale yellow	0·6-1·68	Lewkowitsch
,,	,,	of rank odour	.	2·4-4·6	Parry
,,	,,	Japanese [2]	...	2·3-2·8	Bull

[1] *Journ. Soc. Chem. Ind.*, 1893, 607.
[2] Mann (*Journ. Soc. Chem. Ind.*, 1903, 1357) records 7·18 per cent of unsaponifiable matter for an oil of the saponification value 186·7 (!)

The following table shows the proportions of unsaponifiable matter found in some liver oils other than cod liver :—

Liver Oils.		Unsaponifiable.	Observer.
		Per cent.	
Shark liver oil .	Yellow, steamed	5·27	Fahrion
,,	Red	4·44	,,
,,	Yellow	1·24	,,
,,	Yellowish-red	0 93	,,
,,	Japanese	2·82	Allen
,,	Crude	8·70	,,
,,	Refined	0 70	,,
		10 25	·,
		17 30	,,
		10 31	,,
,,	Pale yellow, from } Scymnus borealis }	10 20 .	Lewkowitsch
,,	Japanese shark	14 1 21 5	Bull
Coal-fish liver oil		6 52	Mann
Tunny fish ,, ,,		1·0-1 8	Fahrion
Ling ,, ,,	. .	2 23	Bull
Haddock ,, ,,	...	1·1	Lewkowitsch
Saith ,, ,, (coal-fish)	...	1 8	,,

Adulteration with mineral oils is readily ascertained by the determination of the saponification value and of the unsaponifiable matter, and by the examination of the latter. Vegetable oils are best detected by the phytosteryl acetate test, as the iodine value obviously does not furnish decisive results, although it may give the first indications, if adulteration with oils having iodine values of less than 120 has taken place.[1] Confirmation of the presence of vegetable oils other than linseed oil [2] may also be obtained by the bromide test. In this connection it should be noted that cod liver oil substitutes are now being sold consisting of a mixture of genuine cod liver oil and iodised sesamé oil (Vol. III. Chap. XV. " Iodipin "). Such artificial cod liver oils will yield much less ether-insoluble bromide than a genuine oil does.

The detection of other liver oils in cod liver oil constitutes, in the present state of our knowledge, a very difficult problem. The determination of the unsaponifiable matter would appear to afford some guidance as to adulteration with other liver oils.

As a rule, other liver oils in commercial cod liver oil can be detected by the taste alone. Thus the ordinary pollock or coal-fish liver oil (saith oil, sej liver oil) has so unpleasant a taste that it cannot be admixed with cod liver oil without injuriously affecting the taste of the latter. But it should be noted that in the year 1903, when the prices of cod liver oil were exceptionally high, the liver oil of the pollock or coal-fish (saith oil) was actually prepared by the steam process,

[1] A cod liver oil substitute is sold under the name of "Fucol" ; it is prepared by digesting marine algæ with a vegetable oil (Zeitschr. f. angew. Chem., 1904, 397). English patent 2081, 1904.

[2] Tollner, United States patent 765, 943.

and such oil was largely added on the Continent to medicinal cod liver oils. 'It is within the author's experience that such steam extracted " saith oil " was offered even in this country as cod liver oil.

The bromide test also would lead to useful results, since the examination of shark liver oil in the author's laboratory has shown that the fatty acids yielded from 12·7 per cent to 15 per cent of ether-insoluble bromide only, as against 30 per cent in the case of genuine cod liver oil.

Shark liver oil, if present in considerable quantities, may also be detected by the isolation of cetyl alcohol, since shark liver oil contains varying proportions of spermaceti (cp. p. 440).

Of fish oils which may be used for the adulteration of cod liver oil the only oil that can be considered here, in the present state of the fish oil industry, is *salmon* oil, as all others, such as menhaden oil, herring oil, and sardine oils, are of too dark a colour and have too unpleasant a taste ; but even salmon oil would betray its presence by a dark colour and inferior taste. Of the *blubber oils* only the best qualities of seal oil and whale oil could be used for adulteration. Their presence, if their quantities are not very large, would not be indicated with any degree of certainty by the iodine absorption and the bromide tests. In case adulteration with seal oil or whale oil be suspected, and the chemical tests fail to furnish a decisive answer, the taste must be considered as one of the most important adjuncts in the detection of the adulterant or adulterants.

Since the detection of fish and blubber oils in cod liver oil is not always possible by means of the quantitative reactions, a number of *colour tests* have been recommended. I have examined the tests proposed by *Kremel, Meyer, Roessler, and Unger*,[1] but as I have found them useless, they are not described here. The colour test, however, described on p. 442, allows to differentiate fish and blubber oils from liver oils.

Notwithstanding the observations made by *Thomson and Dunlop*, and recorded above (p. 423), I would still recommend the sulphuric acid test as a reliable and rapid means of discriminating cod liver oil (and indeed all other fish liver oils) from fish oil (body oil) and blubber oils. It would, of course, not be permissible to judge by the depth of the blue-violet tint obtained with a sample of oil, as to whether adulteration with fish or blubber oil had taken place.

The **British Pharmacopœia** gives the sulphuric acid test as a reaction for the identity of cod liver oil. It has already been pointed out that this test indicates only impurities which are due to lipochromes and colouring matters that have passed from the cellular tissue of the liver into the oil, and further that with the improvement in the manufacturing processes the quantity of these by-products has decreased, so that during latter years the better class oils showed the sulphuric acid colour reaction much more faintly than the liver oils prepared by the old

[1] See second edition of this work, p. 486. Cp. also Wiebelitz, *Pharm. Zeit.*, 1903, 363. Unger's test actually indicated impurities due to decayed livers, which are at present carefully excluded.

processes   This is shown by the fact that a fresh cod liver oil which
had a very slight taste and gave a very strong blue colour with sulphuric
acid showed after standing three years a dark brown colouration with
sulphuric acid, and had a very rancid taste, although the colour of the
oil was unchanged.   This seems to show that with age and the setting
in of rancidity the chromogenic substance giving a blue colour is
destroyed.   Indeed, the strongest colour reaction is given by shark
liver oil, in the preparation of which little care is taken to prevent
decay or putrefaction.   A manufacturer should therefore endeavour to
produce a cod liver oil which does not show the sulphuric acid test at
all, or only very faintly.

The *British Pharmacopœia* prescribes the sulphuric acid test to be
applied to the oil itself.   The form in which this test is prescribed
by the *German Pharmacopœia* is much preferable :—Dissolve one drop
of oil in twenty drops of carbon bisulphide and add one drop of con-
centrated sulphuric acid, when a beautiful violet-blue colour appears at
once, changing afterwards into red and brown.   This test, however,
cannot serve as an identity reaction, since other liver oils give the same
violet-blue colour.   Cod liver oils (as also other liver oils) which have
become rancid, do not show the violet-blue, but give at once the red
colouration ;   oxidised cod liver oil gives a brown colour only.   Thus
an excellent cod liver oil which shortly after having been manufactured
showed a bright violet-blue colouration in the sulphuric acid test, gave
a dark brown colour in the same test a year later, although it had been
kept protected from light and air.

The *United States Pharmacopœia* prescribes carbon tetrachloride in
place of carbon bisulphide.

The detection of fish and blubber oils that have been fraudulently
admixed in smaller or larger quantities with cod liver oil is, in the
present state of our knowledge, still an unsolved problem.   Seal and
whale oils yield much smaller proportions of ether-insoluble bromides
than cod liver oil, as has been ascertained by *Walker and Warburton*
in the author's laboratory.   But Japanese fish oil and a deodourised
fish oil have given numbers ranging from 23 per cent to 39 per cent of
insoluble bromides, so that it is easy to prepare mixtures of cod liver
oil, fish oil, and blubber oil yielding the average percentage of ether-
insoluble bromides furnished by genuine cod liver oil.   At present
exact chemical methods for the detection of these adulterants are still
wanting.   The organoleptic method must therefore be relied upon to
guide in the examination of a suspected sample.

For the determination of the amount of **iodine** in cod liver oil or
iodised cod liver oil, *Stanford* [1] saponifies 300 grms. of oil with 40 grms.
of caustic soda (free from iodine), evaporates to dryness and incinerates
the soap in a porcelain crucible.   The charred mass is next boiled out
with water, filtered, and the filtrate evaporated to 300 c.c.   30 c.c.

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[1] *Pharm. Journ.* (3) 14, 353.

of this solution aro then shaken with 12 c.c. of carbon bisulphide after a few drops of nitrosulphuric acid havo been added (prepared by passing nitrous acid, ovolved on heating starch or arsenious acid with nitric acid, into sulphuric acid). The amount of iodine dissolved in the carbon bisulphide is estimated colourimetrically by comparing the tint with that of another solution prepared similarly from a known amount of potassium iodide.

On shaking pure cod liver oil with water or alcohol no iodine passes into solution ; fraudulently added potassium iodide can thorefore thus be detected.

The best qualities of cod liver oil, as has been pointed out already, are used in pharmacy and for feeding calves. In order to mask the unpleasant taste which tho older medicinal oils had—and which they are popularly believed to have still—various preparations are made from cod liver oil, such as effervescent cod liver oil or emulsified cod liver oils.[1]

For the preparation of theso emulsions *Bomer*[2] states that the emulsions should contain not less than 39-40 per cent of cod liver oil. He also recommends for sweetening the emulsion in addition to glycerin 0 02 per cent of saccharin. Sugar used as such does not keep in the warm weather. He recommends as a preservativo 10 per cent of glycerin and 3 per cent of alcohol. These, as also other substitutes for cod liver oil, such as iodised oils, phosphorised cod liver oil, and " fucol," will be described in Chap. XV.

Lower qualities, *i.e.* the commercial cod oils, the coast cod oils, are used by tanners and curriers (see Chap. XVI. " Sod Oil ").

In the examination of **commercial cod** oil for tanning and currying purposes, the amount of free fatty acids and unsaponifiable matter does not play the same important part as in the examination of medicinal oil.

As the livers which are worked up for cod oil are not worked in the freshest state (sometimes even in a putrid condition), the amount of free fatty acids is considerable, and rises up to 25 per cent and more. The lower the amount of free fatty acids, the higher is the commercial value of tho oil. With regard to acid value Turnbull says : " Oils having high acid value are found to spue readily if used for currying, and they are not at all suitable for chamoising." The amounts of unsaponifiable matter occurring in brown cod oils may be gathered from the following table :—

[1] Cp. Sheard, English patent 492, 1908 ; cp. also K. Kawai and Z. Miwa, English patent application 15,403, 1912.
[2] *Apoth. Zeit*, 1909, 211.

Unsaponifiable Matter in Cod Liver Oils

Description of Oil.				Colour.	Unsaponi- fiable.	Observer.
					Per cent.	
Commercial oil, English	.		.	Yellowish-red	2 62	Fahrion
,, ,, ,,				Pale Yellow	0 6-1 68	Lewkowitsch
Brown cod oil[1]	.	.	.	Brown	1 82	Fahrion
,, ,,	.		.	,,	2 23	,,
,, ,,	.		.	,,	2 68	,,
,, ,,	.	.	.	,,	2 0-5 3	Lewkowitsch
,, ,,	.	.	.	,,	1 87	Thomson and Ballantyne
,, ,,	.	.	.	,,	7·3 (!)	Bull

Cod oil is frequently adulterated with fish oils, the detection and quantitative determination of which still offer a difficult problem, which has not been solved satisfactorily.

For a method of examination of cod liver oil by means of its misci- bility curves with acetone, the original papers by *E. Louise* should be consulted.[2]

As cod liver oil, like fish oils, absorbs oxygen, the employment of it for paints and varnishes has been frequently suggested and also patented. Since the unsaturated fatty acids differ materially from those of linseed oil, no flexible skin can be obtained from cod liver oil. All these proposals are therefore valueless, although when prices of linseed oil are high, adulteration of " boiled oil " with liver (and fish and blubber) oils is frequently practised.

Procter and Holmes [3] have examined the oxygen absorption of cod liver oils and obtained the results stated in the following tables :—

Medicinal Cod Liver Oil

Blown	Specific Gravity	Refractive Index	Iodine Value
Hours			
0[4]	0 921	1·4814	163·0
4	0 934	1 4819	163·0
8	0·937	1·4825	139·5
12	0 940	1 4831	131·5
16	0 952	1 4836	127 0
20	0 963	1·4847	122·0
24	0·969	1·4848	117·0

[1] Bull found 7·3-7·9 per cent of unsaponifiable matter in some brown oils. These figures suggest the presence of other liver oils.

[2] *Journ. Pharm. Chim.*, 1911, 377.

[3] *Journ. Soc. Chem. Ind.*, 1905, 1287.

[4] Original oil.

Cod Liver Oil

Blown	Specific Gravity. 15° C	Refractive Index. 15° C	Iodine Value.
Hours			
0 [1]	0 930	1 4812	156·0
3	0.930	1·4815	155·0
6	0·935	1·4820	152 0
9	0 937	1 4820	151·0
12	0 938	1·4825	150 0
15	0 940	1·4827	148 0
18	0 943	1·4828	145 0

Cod Oil

Blown.	Specific Gravity. 15° C.	Refractive Index. 15° C.	Iodine Value.
Hours.			
0 [1]	0 923	1 4810	154 0
3	0 928	1 4813	148·0
6	0·928	1 4815	148·0
9	0·928	1·4819	146 0
12	0 930	1·4819	144·0
15	0 930	1·4820	143·0
18	0·931	1·4822	143·0
21	0·932	1·4827	142·0
24	0·934	1·4828	141·0

Other liver oils are commercially of minor importance, and therefore need not be considered here individually. In the following table (see table facing p. 447) I collate the characteristics of some oils.

Shark liver oil appears to be no longer used in this country; at any rate it is not extracted here commercially. This oil is, however, prepared in considerable quantities in Iceland, and exported to the Continent for use in tanning; it is also manufactured at the coast of California, the coarser grades being employed in the making of tarpaulins and other oiled cloth. In admixture with linseed oil and glue, shark liver oil is used in the preparation of plastic masses and rubber substitutes.[2] The livers from any shark caught by the trawlers are extracted, together with other livers, and therefore the " Coast Cod Oil " (p. 429) will contain varying quantities of shark liver oil.

Dogfish liver oil is prepared from *Squalus acanthias*, L. (" Spiny dogfish "), according to *G. F. White* from *Mustelus canis*. This fish is caught off the coasts of Oregon, Washington, and British Columbia in large quantities. One hundred livers are stated to yield from 6 to 8 gallons of oil. The oil is not generally kept separate from cod liver oil, and is sold in admixture with the latter for currying purposes.

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[1] Original oil.
[2] R. Zimpel, German patent 236,728.

Tho name " dogfish " is also given to other species of fish closely allied to shark, such as *Scyllum laticeps, Acanthias vulgaris,* L. (spined dogfish), *Lanina glauca* (tiger shark), *Mustelus canis* (dogfish).

In order to protect the fisheries the Federal Government of Canada offers a bounty for the capture of the dogfish, which on account of its voraciousness has become a serious menace to fisheries on the East Coast ; hence considerable quantities of dogfish oil and dogfish " scrap " are obtainable in commerce.[1]   The production of dogfish oil in Nova Scotia has recently reached large proportions, 700,000 fish being worked up in the season 1910.

The changes which skate liver oil, coal-fish liver oil, and shark liver oil undergo on blowing with air at about 100° C. are set out in the following tables due to *Procter and Holmes* [2] :—

Skate Liver Oil

Blown	Specific Gravity. 15° C.	Refractive Index. 15° C.	Iodine Value.
Hours			
0 [3]	0·926	1·4830	187·0
3	0·926	1·4830	185·0
6	0·926	1·4830	185·0
9	0·927	1·4831	174·0
12	0·929	1·4834	167·0
15	0·929	1·4835	163·0
18	0·930	1·4837	162·0
21	0·933	1·4840	160·0
24	0·937	1·4843	159·0

Shark Liver Oil

Blown	Specific Gravity. 15° C.	Refractive Index. 15° C.	Iodine Value.
Hours.			
0 [3]	0·910	1·4750	120·0
3	0·911	1·4752	119·0
6	0·911	1·4752	117·0
9	0·912	1·4754	111·0
12	0·913	1·4759	110·0
15	0·913	1·4760	108·0
18	0·913	1·4760	105·0
21	0·913	1·4760	104·0
24	0·916	1·4762	103·0

[1] *Canada, Department of Agriculture Central Experimental Farm, Ottawa, Ontario,* 1906, p. 158 ; 1907

[2] *Journ. Soc. Chem. Ind.*, 1905, 1287.

[3] Original oil.

Liver Oil from	French.	...vity.	Solidifying Point.	Specifi... M...Tempera... Reactio...
Skate . . .	Huile de foie d'ange (d'angelot)	Meere... 15° C.)	..	..
		15° C.)	..	322
„ (Japanese Suketo-fura)	..	15° C.)	..	..
Tunny . . .	Huile de foie de thon	Thunf 15° C.)	..	..
„ (Japanese Maguro)	..		..	
Haddock [3] . .	Huile de foie d'égrefin	Schell 15° C.)	..	..
		0	..	300
			..	257
Coal-fish [6] (Pollock), saith .	Huile de foie de merlan vert, ou sey, ou charbonnier	Seileh lebe... 15° C.)	..	..
		15·5° C.)	..	..
		15° C.)	..	..
Ling . . .	Huile de foie de lingue	Leng 0	..	234
		15 5° C.)	..	..
Shark (Arctic) .	Huile de foie de requin arctique	Harfi 15° C.) 18° C.)	..	..
„ (Arctic) .		tas 9130	..	..
„ (Sand) .	..		..	..
„ (Hammerhead)	..		..	..
„ (Japan) .	(Japon)	9177	..	..
„ (Japan) .	..	8	..	..
„ (Spotted shark) .	..	40° C.)	..	..
„ (Torpedo) .	..		..	..
„ (Squeteague)	..		..	..
Ray .	Huile de foie de raie	Roch 15·5° C.) 15° C.)	..	..
	Huile de foie de pastenague	Stack 15° C.)	..	..
Eagle ray . .	Huile de foie d'aigle de mer	Adle 15° C.)	..	..
White sting ray [14]	..	40° C.)	..	..
Shark ray . .	..	40° C.)	..	..
Hake . .	Huile de foie de merlus ordinaire	Sech 56 15·5° C.) (Re 54	..	..
Scup . . .	..		..	..
Eel . . .	..		..	317
Whiting .	Huile de foie de cyprin	Wers 90 79	..	..
Dog-fish . .	Huile de foie de roussette (chien de mer)	Hun 20	..	..
		15° C.)	..	..
Brusnier, Cusk	..	22 Tors 15·5° C.) Bros	..	..
„ „ .	Huile de foie de lanne	Bros 58	..	..
Common saw fish	..	40° C.)	..	..
Butter fish . .	..		..	..
Trout . . .	..	For... 15·5° C.)	..	..

[1] Chem. Rev., 1913, 72
[2] Chem. Rev., 1913, 71   The aut... oil (see table facing page 423).
[3] This oil is frequently termed c...

06, 390.
...meter index of insoluble
...ion – 0·5° in a 200 mm. t...
...gleberthran."

pp 1...

1·6 per

Coal-Fish Liver Oil

Blown.	Specific Gravity. 15° C.	Refractive Index. 15° C.	Iodine Value.
Hours			
0 [1]	0·921	1·4786	153·0
3	0·921	1·4787	151·0
6	0·921	1·4788	146·0
9	0·922	1·4788	141·0
12	0·923	1 4789	136 0
15	0 924	1 4790	135 0
21	0 927	1 4792	134·0
24	0 931	1·4794	130 0

Some characteristics of these liver oils and of other lesser known liver oils are given in the table opposite.

Two qualities of skate liver oil, viz. medicinal oil and technical oil, are being placed on the market by the commissioner of Fisheries, Bengal.

The livers of the crustacea (*e.g. Cancer pagurus, Palinurus vulgaris*) as also the livers of decapods (*Birgus latro*) are very rich in oil. An examination of these oils has not been carried out hitherto.

With regard to fats from pig and ox liver, see " Animal Fats."

Lesser known liver oils, see table opposite.

γ. Blubber Oils

In this group are comprised oils of different composition. Seal oil, whale oil, turtle oil, and dugong oil consist almost wholly of glycerides ; dolphin oil, porpoise oil, and brown fish oil contain notable amounts of spermaceti, forming, as it were, intermediate members between true fatty oils and liquid waxes.

The last three members of this group — dolphin, porpoise, and brown fish oils — occupy an exceptional position on account of their containing considerable proportions of glycerides of volatile acids. In this respect turtle and dugong oils form intermediate links between these oils on the one hand, and seal, and whale oils on the other.

[1] Original oil.

SEAL OIL

French—*Huile de phoque.* German—*Robbentran, Seehundstran.*
Italian—*Olio di foca.*

For tables of characteristics see pp. 450–152.

Seal oil is obtained from the blubber of the various species of seal,
such as *Phoca vitulina, Phoca grœnlandica, Phoca lagura, Phoca caspica,*
etc.

The following seals occurring in the Antarctic Ocean have been
described recently (National Antarctic Expedition, 1901–4, *Natural
History*, vol. ii. Zoology, London, 1907), Weddell's seal (*Leptonychotes
Weddelli*), sea-leopard (*Stenorhynchus leptonyx*), crab-eating seal (*Lobodon
carcinophagus*), Ross's seal (*Ommatophoca rossi*), elephant seal (*Macror-
hinus leoninus, M. angustirostris*), in commerce the oil is also named
sea-elephant oil, Hooker's sea lion (*Arctocephalus Hookeri*).

In the early times of "whaling," the oil was exclusively "tried"
on board the whaling vessels, just as in the case of whale oil (see p. 455).
Later, the seals were brought to rendering establishments on shore,
and the blubber cut from the animal was thrown into large vessels of
great height, in which the oil was pressed out from the lower layers
by the superincumbent weight of the blubber, and the exuding oil was
allowed to run off continuously. The oil running out at first was pale,
and almost free from smell. When, however, the blubber became
rancid and even putrid, the oil obtained was rich in free fatty acids,
and acquired, besides a dark colour, a nauseous taste. At present,
seal oil is recovered by more modern methods,[1] such as are described
under the heading "Whale Oil," p. 454.

According as the oil is extracted from fresh blubber on board the
steamer, or from blubber which has been brought to shore, the colour
of seal oil varies.

The crude seal oils deposit "stearine" on standing, which is removed
by filtering the oil. The "stearine" is sold as "fish stearine" or
"fish tallow" for soap-making and currying purposes. The "stearine"
from the first run is white and almost free from odour, whereas the
"stearine" obtained from the last rendered oil is dark, high in its
proportion of free fatty acids, and of bad odour. This "stearine"
blackens easily on exposure to the atmosphere.

In commerce four qualities of seal oil are differentiated—water-
white, straw, yellow, and brown seal oil; these represent the oils as
they are obtained successively from the blubber by "rendering."
The darkest quality is that which has been the longest in contact with
the animal tissue, and has been extracted at the highest temperature.

The oil from *Phoca fœtida* (German—Ringelrobbe), occurring in
the Baltic, notably differs from the seal oils furnished by the marine
seals in respect of the iodine value. This must be attributed to the

[1] Cp. Osmundsen, English patent 2357/1912.

influence of food conditioned by the fauna of an inland sea.[1] Such influence becomes more pronounced still in the case of the seal oil from *Phoca fœtida,* var. *saimensis Nordkvist,* a variety of seal which has adapted itself for many generations to the fresh water of the Saima Lake.[2]

According to *Ljubarsky*[3] the mixed fatty acids from the *Caspian* oil consist roughly of 17 per cent of palmitic acid and 83 per cent of liquid acids. The latter yielded on oxidation a mixture of dihydroxypalmitic and dihydroxystearic acids, from which the presence of oleic acid and physetoleic acid (or hypogeic acid) in the original oil was inferred. *Ljubarsky* found no linolic acid, the presence of which had been recorded by *Kurbatoff*[4]

Walker and Warburton obtained in the author's laboratory, however, in the bromide test 27·54-27·92 per cent of ether-insoluble brominated glycerides ; the fatty acids yielded only 19·8-19·9 per cent of insoluble bromides, which behaved like the brominated products obtained from fish and liver oils. *Tolman* found 19·5 per cent insoluble bromides in a specimen of seal oil yielding (by the lead-salt-ether method) 9·96 per cent solid acids.

Bull isolated from a specimen of northern seal oil a liquid fatty acid absorbing 306·8 per cent of iodine.

In the elaidin test seal oil gives a pasty mass, which separates from a liquid portion.

The following table records the proportions of free fatty acids and unsaponifiable matter found by several observers : —

No	Kind of Seal Oil	Free Fatty Acids (as Oleic Acid)	Unsaponifiable Matter	Observer
		Per cent	Per cent	
1	Water-white	0 2		Lewkowitsch
2	Pale	0 9-1·5		,,
3	Cold drawn, pale	1 80	0 5	Thomson and Ballantyne[5]
4	Steamed, pale	1·46	0 38	,,
5	Tinged (brown)	8 29	0 42	,,
6	Norwegian	7 53	0 51	,,
7	Northern	3 2	1 05	Bull
8	Very pale	0 98-1·13		Chapman and Kolte[6]
9	Yellow	1 41	..	,,
10	Light brown	4 09	...	,,
11	Dark brown	19 95	...	,,

It may be noted that *Thomson and Dunlop* obtained with an undoubtedly genuine and fresh seal oil a distinct violet colouration with sulphuric acid, similar to that given by liver oils. This specially prepared seal oil had the specific rotatory power $[a] j = -0·19$.

[1] Cp. Lewkowitsch, *Jahrbuch d. Chem*, 1905, (xv.) 420.

[2] This seems to me hardly tenable as a general proposition, inasmuch as carp fish oil has an iodine value of 84 only (cp. also my remarks in *Jahrbuch d. Chem.,* 1903, xiii. p. 406 ; 1904 (xiv.), 440).

[3] *Journ. f. prakt. Chem.,* 1898, 26.   [4] *Berichte,* 25, Referate, p 506.

[5] *Journ. Soc. Chem. Ind.,* 1891, 236.   [6] *Ibid.,* 1891, 843.

Physical and Chemical Characteristics of Seal Oil

Source	Specific Gravity			Solidifying Point		Saponification Value		Iodine Value	
	°C.		Observer	°C	Observer	Mgrms KOH	Observer	Per cent	Observer
Phoca groenlandica	15	0·925	Kremel	Deposits "stearine" at 3	Schaedler	189-196	Stoddart, Deering	162·6	Thomson and Dunlop
	,,	0·9249-0·9263	Chapman and Rolfe			178-179	Kremel	127-128	Kremel
	,,	0·9244-0·9261	Thomson and Ballantyne	-2 to -3	Jean	189·3-192·8	Thomson and Ballantyne	142·2-152·4	Thomson and Ballantyne
						190·7-196·2	Chapman and Rolfe	130·6	Lewkowitsch
								129·5-141·1 [1]	Chapman and Rolfe
								147·1	Bull
								147·5	Lewkowitsch [2]
								184·8	Schneider and Blumenfeld
Phoca foetida	15	0·9825	Schneider and Blumenfeld	...	...	188·2	Schneider and Blumenfeld		
Phoca foetida var. saimensis Nordkvist	15	0·9321-0·9336	,,	...	...	188·5-189	,,	191·4-193·3	Blumenfeld ,,

[1] The bromine values of the specimens were 69·6 - 80, corresponding to iodine values 110·5-126·7.
[2] Water-white seal oil.

Physical and Chemical Characteristics of Seal Oil—continued

	Reichert Value.		Reichert-Meissl Value.	Specific Temperat. Reaction.		Refractive Index.			
	c.c. 1/10 norm KOH.	Observer.			Observer.	1·4776	Tolman [1]		
						Oleo-refractometer.			
						"Degrees."	At ° C.	Observer.	
Phoca grœnlandica	0·67-0·22	Chapman and Rolfe		212-229	Thomson and Ballantyne	−8	22	Jean	
						−15	22	,,	
						−30 to −36	22	Pearmain	
						−32	22	Dowzard	
						Buty-ro-refractometer.			
						72·7	25	Liverseege [2]	
						64·0	40	,,	
						74·0	25	Lewkowitsch [3]	
						65·0	40	,,	
						76·2	25	Thomson and Dunlop	
						85·9	20	Schneider and Blumenfeld	
						75·3	35	,,	
						87	20	,,	
						78·4	35	,,	
Phoca fœtida			1·12-1·69	...	Schneider and Blumenfeld				
Phoca fœtida var. saimensis Nordkvist			0·96-1·55	...	,,				

[1] *Journ. Ind. and Eng. Chem.*, 1909, 340.
[2] *Analyst*, 1904, 210. The Valenta test of the sample was 85° C.
[3] Water-white seal oil.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Acids+Unsaponifiable		Specific Gravity		Solidifying Point		Melting Point	
	Per cent	Observer	At 15° C.	Observer	°C	Observer	°C	Observer
Phoca groenlandica	95·45 92·8-94·2	Kremel Chapman and Rolfe	...	...	15·5-15·9 Titre	Lewkowitsch	22-33	Chapman and Rolfe
Phoca foetida	95·8	Schneider and Blumenfeld	0·9156	Schneider and Blumenfeld	17	Schneider and Blumenfeld	·	·
Phoca foetida var. saimensis Nordkvist	95·6-95·85	,,	0·9172	,,	13-14	,,	14	Schneider and Blumenfeld

Physical and Chemical Characteristics of the Insoluble Fatty Acids—continued

Neutralisation Value		Iodine Value		Refractive Index Butyro-refractometer		
Mgrms KOH	Observer	Per cent	Observer	At ° C.	Degrees	Observer
190·4-196	Chapman and Rolfe	...	·	40	49·7	Lewkowitsch
196·5	Schneider and Blumenfeld	186·5	Schneider and Blumenfeld	20 35	74 62·3	Schneider and Blumenfeld
196-198	,,	195·3-201·8	,,	20 35	74·1 64·8	,,

The elephant seal caught on the coasts of Kerguelen Island yields a light yellow oil having the following characteristics [1] :—

	0. Light Yellow	1 Light Yellow	1. Light Yellow	2 Red Yellow	2 Red Yellow	Red Brown
Specific gravity at 15° C	0 9222	...	0 9223	0 9215	.	.
Saponification value	189 0	190 0	190 0	189 4		
Iodine value . .	124 0	.	130 9	124 2		
Insoluble fatty acids + unsaponifiable . .	. .	. .		95 0		
Free fatty acids, per cent	1 48	0 98	0 76	1 70	8 00	24 00

The oil is contained in a thin layer of blubber, each seal yielding about 80 kg. of oil. The oil deposits " stearine " on cooling to 10-15° C. ; below 10° it becomes pasty and has a higher solidifying point than that of ordinary northern seal.

Sea lion oil [2] obtained from *Otaria stelleri* Less. (Japanese name " Ashika ") is a yellow liquid having a fishy smell. An examination of this oil by *Tsujimoto* showed the following characteristics :—

Specific gravity	0 9278
Saponification value . .	189 80
Iodine value . .	156 37
Acid value . .	0 58
Refractive index at 20° C.	1 4783
Butyro-refractometer . .	80 0
Melting point of fatty acids, ° C.	29·5

The ether insoluble bromides of the total fatty acids amounted to 36·04 per cent ; these bromides after extraction with benzene contained 70·76 per cent of bromine.

The best qualities of seal oil are used as burning oils in lighthouses, or when prices of cod liver oil are high, as an adulterant of cod liver oil ; seal oil having a similar composition to cod liver oil and possessing even less taste and smell, there is no reason why it should not replace to some extent cod liver oil in pharmacy [3]. Lower qualities of seal oil are used in soap-making, particularly soft soaps, and in the leather industries. The changes which seal oil undergoes in the sod oil manufacture is described in Chap. XVI.

The change suffered by seal oil on blowing with air at 100° C. is stated in the following table, due to *Procter and Holmes* [4] —

[1] J. Lund, *Seifensieder Ztg.*, 1912, 451.
[2] Tsujimoto, *Chem. Revue*, 1913, 71.
[3] A. Wingard, *Svensk. Farm. Tidskr.*, 1911, 10.
[4] *Journ. Soc. Chem. Ind.*, 1905, 1287

Pale Seal Oil

Blown	Specific Gravity	Refractive Index.	Iodine Value
Hours			
0[1]	0·932	1·4795	121·5
4	0·941	1·4798	121·5
8	0·955	1·4800	105·5
12	0·956	1·4808	100·0
16	0·961	1·4815	96·5
20	0·961	1·4820	91·5
24	0·968	1·4820	91·5

Seal oil is frequently adulterated with mineral oils and rosin oils, the detection of which is, however, easy. A mixture of seal oil with various fish oils is frequently sold as seal oil. The detection of the adulterant is not easy, as neither the iodine value nor the bromide test furnish decisive indications. In the present state of our knowledge the taste and smell render some assistance in the examination

WHALE OIL

French—*Huile de baleine.*   German   *Walfischtran.*
Italian—*Olio di balena.*

For tables of characteristics see pp. 460, 461.

Whale oil is extracted from the blubber of various species of the genus *Balœna*, viz. *Balœna mysticetus*, Greenland or " Right " whale (northern whale oil), which attains a length of about 60 ft., its head being about one-third of its length ; *Balœna australis* (southern whale oil),[2] this animal attains a length of about 45 ft. ; *Balœnaoptira longimana* ; *Balœnaoptira musculus*, common rorqual (Fin-back oil) (Finner whale oil)—French : Huile de rorqual ; German : Finnfischtran— attains a length of about 70 ft. and is found all over the world ; *Balœnaoptera borealis*, Northern or Ruolphis rorqual, measuring about 40-50 ft. is found principally off Scotland, Faroe and Falkland Islands ; Bottle-nose whale, *Balœnoptera hyperoodon* and Blue whale, *Balœnaoptera sibbaldii*,[3] this latter is said to be the largest living animal in the world, and sometimes attains a length of 100 ft. ; *Neobalœna marginata* ; *Rhachianectes glauca*, Cope (Japan). The northern whale oil is the " train oil " proper ; but this name has become a generic

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[1] Original oil.

[2] T. E. Salvesen, *Journ. Royal Soc. of Arts*, 1912, 515.

[3] The *Discovery* (National Antarctic Expedition, 1901–4), *Natural History*, vol. ii, Zoology, London, 1907) found no traces of the southern Right whale (*Balœna australis*) which Captain Ross had reported to be abundant in the 'forties of the last century, but met with the rorqual, the Australian whale (*Neobalœna marginata*), the " killer," and two new cetaceans.

name, and has been extended to all other " blubber oils " included in this group. For the milk fat of whales, cp. table under " Butter fat."

The blubber of whales caught in the northern seas of Europe was, in the early days of the whaling industry, " tried " on board the whalers, but in consequence of the low yield and also of the low quality of oil thus obtained, the whales are now brought into the " trying " stations situated in Finnmarken, on the Lofotes, Faroe, Shetland, and Hebrides Islands, and in Iceland.

To a large extent the American whalers still " try " the blubber on board ship and deliver the crude oil into the refineries of New Bedford, Mass., on the east coast, and of San Francisco on the west coast. In British Columbia the most modern methods of collecting and refining whale oil are employed.

The whales caught in the whaling grounds adjacent to the South African coast, especially to that of Natal, are brought into the " trying " stations at Durban and Salvanha Bay (Hootjes Bay).

The " right whale " oil is of better quality than the " southern whale " oil. The " finner whale " oil is of still lower quality. Hence the finner whale was formerly neglected by the whalers, but at present even this kind of whale is eagerly pursued by them along the coasts of Norway and Newfoundland, especially off South Africa, as also to a smaller extent on the Asiatic coast of Russia, and the coast of Japan.

Besides the species of whales named, other kinds, such as the " orca " or " killer " whale, the " beluga " or white whale, are caught, especially by the American whalers, and the blubbers are rendered for whale oil.

The average yield of oil obtainable from the different species of whales is given in the following table :—

Kind of Whale.		Yield in Barrels of 31.5 gallons.
Right whale, Pacific	.	25 to 250
Right whale, Atlantic	.	25 ,, 150
Bowhead whale	.	30 ,, 250
Humpback whale, Pacific	.	10 ,, 110
Humpback whale, Atlantic	.	10 ,, 100
Finback whale, Pacific		10 ,, 70
Finback whale, Atlantic	.	20 ,, 60
Californian gray whale	.	15 ,, 60
Orca or killer whale		1 ,, 6
Beluga or white whale	.	1 ,, 3

The " sulphur-bottom " whale found off the coast of British Columbia yields about 6 tons of oil, $3\frac{1}{2}$ tons of body bone, $3\frac{1}{2}$ tons of guano and 3 cwts. of whale bone. These whales are said to be worth £100 each, whereas the " right whale " is much rarer and is valued at about £2000.

The extraordinary small quantity of cod fish caught off the coast of Norway in 1903, caused those interested in the cod-fishing industry to start an agitation with the object of enforcing legislation against the killing of the whale off the coast of Norway, as the whales drive away the seals, which work the greatest destruction amongst the cod

shoals. In consequence of this agitation a law was passed, which came into force on January 1, 1905, forbidding the killing of whales within Norwegian Sea territory and the landing of whales in the Norwegian rendering establishments. This will, no doubt, increase the output of the rendering works in the Faroe, the Shetlands, and the Hebrides Islands [1] It is doubtful whether this legislation will improve the yield of the fishes, as the causes of the migration of the fish shoals are at present unknown to us.

According to the equipment of the blubber-rendering stations the yield of the oil and also its quality vary. In the most modern works the blubber is stripped clean from flesh immediately after the arrival of the whaler, and care is taken to leave as little flesh as possible on the blubber. The latter is then cut into strips, which are thrown into chopping machines, whence the comminuted mass is immediately delivered into melting pans, and boiled with steam.[2] Five different qualities of whale oil are produced. The best quality is the oil which first runs off the blubber at the lowest temperature, and is known in commerce as " Whale Oil No. 0 " ; it is of a pale yellow colour, and has but a faintly fishy smell. This oil contains a very small quantity of free fatty acids. The best brands are water-white, and are free from volatile fatty acids. On further boiling the second quality (" Whale Oil No. 1 ") runs off ; it is a little darker in colour, although still pale yellow. Its fishy smell is more pronounced than the oil of the first running.

These two qualities of oil are stored in large vessels, whereby they become clarified whilst depositing " stearine," which is filtered off, pressed in hydraulic presses, and sold as " whale tallow," " whale stearine " for soap-making. When tallow is high in price, it is sometimes adulterated with whale stearine ; this will be detected by the high iodine value of the liquid fatty acids, and also by the yield of insoluble bromides.

The residual mass in the boiling pans, together with the flesh of the whale, is cut up into strips or fairly large lumps, and is " tried down " in a digester under a pressure of 40-50 lbs. Thus the oil classed as " No. 2 oil " is obtained. This oil has a brown colour and a strongly developed fishy smell ; its proportion of free fatty acids is considerably higher than in " Oil No. 1." In some stations " Whale Oil No. 2 " is made from the blubber residues only, and does not contain any oil from the flesh. Hence it represents a superior article to the " No. 2 Oil," described in the preceding lines.

The bones are also worked up in the same manner, and yield a still inferior quality of oil. Such oil (" Whale Oil No. 3 ") is darker still, has a more strongly developed odour, and a high percentage of free fatty acids. " Whale Bone Oil " of commerce is, however, not

[1] In consequence of the "Whale Fisheries (Scotland) Act" of 1907 the Fishery Board have prescribed a closed time for the prosecution of the whaling industry for a period of five weeks, extending from 1st June to 5th July (during the great summer herring fishery), within a distance of forty miles off the coasts of Shetland.

[2] A description of a modern installation for working up whale oil on land is given in *Oil, Paint, and Drug Reporter*, 1907, No. 10.

exclusively made from the bones, except in those cases where the product is sold as " Bone Oil."

The oil obtained after the flesh has undergone some pronounced putrefaction (" Carcase Oil," " Whale Oil No. 4 ") is still darker, and more objectionable as regards smell, and contains a higher proportion of free fatty acids. In the three lowest qualities the proportion of unsaponifiable matter is considerable.

It must, of course, be understood that the different qualities described above, with the exception of " Whale Oil No. 0," vary within wide limits, so that no definite standards can be laid down. Specimens of Norwegian Whale Oils No. 1, No. 2, and No. 3, examined in my laboratory, gave the following acid values respectively :—3 97 ; 20 6 ; 53·42. If the oils have been filtered, they are sold as " Whale Oil, filtered." Even a " Filtered Whale Oil No. 4," occurs in commerce.

In the refining of whale oil the oil is first subjected to a " demargarinating " process by cooling the oil and separating off the stearine in centrifugal machines. The liquid portion is then sometimes deodorised by treatment with superheated steam. The better qualities of whale oil are bleached by means of fuller's earth. Some whale oils can be bleached fairly easily by means of chemicals, but each individual sample presents a separate problem and experiments must be made to see which bleaching agent is the most suitable.

The better qualities, i.e. those prepared from fresh materials, are used for cattle feeding. The residue after the removal of the oil finds a ready market as manure, " whale guano " [1]

This process is thoroughly carried out in Newfoundland (at Balena), where the Government has established several new plants. The carcases of the whale are there completely used up in the manufacture of oil, " stearine," bone meal or bones, and other articles of commerce.

If the whale is landed in a perfectly fresh state, cattle meal can be prepared from the fresh meat, as is being done in Iceland and in the Faroe Islands. Some fresh meat is also consumed locally. The greater part of the whales caught off the coast of Japan and Korea are used as human food, little oil being exported. The following table gives some statistics of the working up of whales in Iceland in the years 1910 and 1911 :—

	1910		1911	
	Quantity (100 kilos)	Value £	Quantity (100 kilos)	Value £
Whale oil	36,473	62,846	26,746	38,278
Whale bone, cwts.	954	3,667	1,021	3,524
Cattle meal	11,377	8,229	7,126	4,940
Guano	8,683	5,435	10,812	5,327
Bones	8,900	3,531	2,833	1,132

[1] *Osmundsen and Osmundsen*, Norwegian patent 21,822 ; German patent 260,857.

The production of oil in South Georgia in 1911 was 106,800 barrels.

The Shetland whaling industry is, in consequence of the above-mentioned Norwegian law, on the increase. The number of whales caught during the season 1904 amounted to 412.

In 1905, 2364 whales were killed near Spitzbergen, Iceland, the Faroe, Shetland, and Hebrides Islands. 72,420 barrels of whale oil are stated (!) to have been produced.

The total production of whale oil amounts at present to 3,000,000 gallons per annum; of these 900,000 are produced by the Norway fisheries, 750,000 by the United States fisheries, and the remainder by Scotland, Russia, Newfoundland, Japan, and other countries.

The following table gives some characteristics of various brands of whale oil. The numbers are due to *Bull* :—

	Specific Gravity at 15° C	Acid Value	Saponific Value	Iodine Value	Unsaponifiable
Antarctic right whale oil (America)	0 9257	0·56	183·1	136 0	1 46
Whale oil No. 1, unrefined (Finmarken)	0 9181	0·86	188 6	101·0	2·36
Refined (Glasgow) . .	0 9211	1·4	181 7	113 2	2 33
Arctic whale oil, refined (America)	0 9234	1 9	185 0	117·4	2·11
Crude white whale oil (America)	0·9222	2·5	183·9	127 1	1·37
Whale oil No. 2, unrefined (Finmarken)	0 9182	3·6	188 3		3·3
Yellow whale oil, refined (Glasgow)	0 9232	10·6	185 9	110 0	1 89
Whale oil No. 3, refined (Finmarken)	0 9162	26·5	185 7	96 0	2·42
Brown whale oil refined (Glasgow)	0·9272	37 2	160·0	125·3	3 22
Whale oil No. 4, unrefined (Finmarken)	0·9205	58·1	182 1	89·0	3·4
Dark whale oil, refined (Glasgow)	0·9170	98·5	178·3	103·1	3·03

The chemical composition of the whale oil fatty acids has not yet been established satisfactorily. The deposited "stearine" consists to a large extent of palmitin. The iodine value of a sample of pressed cake examined in the author's laboratory was 37·9. *Stadler*[1] obtained from a whale oil of the iodine value 89·5, 14·72 per cent of ether insoluble brominated fatty acids. Volatile fatty acids are absent; the high *Reichert* values recorded by earlier observers are undoubtedly due to the specimens examined having been highly rancid.

Hehner and Mitchell obtained from a specimen of whale oil 25 per cent of a brominated glyceride, to which they ascribed the composition $C_3H_5(C_{18}H_{29}O_2Br_6)_2(C_{18}H_{33}O_2Br_2)$. A specimen of whale oil examined in the author's laboratory by *Walker and Warburton* gave only about

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[1] Determined in the author's laboratory.

16 per cent of a highly brominated glyceride, whilst the fatty acids yielded 12·4 per cent of an ether insoluble brommated acid, which behaved like the products derived from other marine animal oils, in that it blackened at 200° C., without melting. This specimen of whale oil was a somewhat old one which evidently had undergone some oxidation, for more recently a number of whale oils examined in my laboratory gave from 20·09 per cent to 22 59 per cent of ether-insoluble brommated acids. Recently *Tsujimoto* found in a freshly prepared whale oil (from *Rhachianectes glauca*) 27·81 per cent of ether-insoluble brommated fatty acids. The fatty acid from which the ether-insoluble bromides were derived has been identified by *Tsujimoto* as clupanodonic acid. The 27·81 per cent of ether-insoluble brominated fatty acids would correspond to 8·39 per cent of clupanodonic acid. This is in excellent agreement with the amount of insoluble bromides found recently by the author for a freshly filtered whale oil of best quality, namely, 27·77 per cent. More recently still amounts of insoluble brommated fatty acids up to 32 per cent have been found by the author.

Bull isolated from a number of whale oils some highly unsaturated fatty acids, having iodine values ranging from 251 to 315·6. The readiness with which low class whale oils become oxidised on exposure to the air may explain the fact that *Fahrion* found from 0·39 to 1·44 per cent of oxidised fatty acids in some specimens.

The amount of unsaponifiable matter also varies with the quality of the oil. The following table contains the amounts of unsaponifiable matter determined in commercial oils. The lower the quality of the oil, the larger the amount of unsaponifiable matter (and the lower consequently the saponification value).

Unsaponifiable Matter in Whale Oils

Description of Oil	Per cent	Observer.
Norwegian, yellowish-red	0 65	Fahrion
,, yellowish-brown	1 26	,,
,, brown	1·37	,,
Pale . . .	1 22	Thomson and Ballantyne
,, refined . .	0 92-3·72	Lewkowitsch
Samples described in table, p. 458	1·4-3·1	Bull

The iodine value of a given specimen of whale oil depends on the amount of " stearine " left in the oil; hence the great variations in the numbers recorded in the tables are readily explained.

Whale oil is not infrequently adulterated with rosin oil, the detection of which is simple. More difficult is the detection of admixed seal oil, on account of the great similarity of the two oils; at present this is practically impossible by chemical means; taste alone permits the recognition of seal oil.

Physical and Chemical Characteristics of Whale Oil

Oil from	Specific Gravity		Saponification Value		Iodine Value		Reichert Value			Maumené Test		Refractive Index		
	°C.	Observer	Mgm. KOH	Observer	Per cent	Observer	Per cent KOH	Observer	°C	Observer	At 20 C	Observer		
											1·4762	Tsujimoto		
											Oleorefractometer			
											At 22 C	Observer		
Balæna and Balænoptera species	15	0·9170, 0·9252	Bull	203·14, 185·5	Doering, Stadtland, Thomson and Ballantyne	110·1	Thomson and Ballantyne, Schweitzer and Lungwitz, Bull	0·5–2·04	Lewkowitsch	8·5–80·1, ·21	Robb Archbutt, Jean	+102·5			
		0·9225, 0·9225	Schweitzer and Lungwitz, Thomson and Ballantyne	188·8, 188·5, 187·0, 194·1	Schweitzer and Lungwitz	121·3, 127·7, 130·92, 117·7	Lewkowitsch			d		+42 to +48	Jean Paumann		
		0·9293										Butyrorefractometer			
									Specific Temperature Reaction		At C	Degrees	Observer	
									155	Thomson and Ballantyne	25, 40, 25	65, 56, 68 9	Leverseege 4, Lewkowitsch	
Rhachianectes glaucus, Cope	15·5	0·9234	Tsujimoto	192·6	Tsujimoto	124·6	Tsujimoto					40, 25, 40	59·3, 68·5, 59·5		

1 Southern whale oil　2 At 100° C light whale.　3 Whale oil No 1 filtered
4 Analyst, 1904, 211　Optical rotation of the sample, +0·5° in a 200 mm tube　Valenta test 106 C　5 Whale oil, No 2

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Specific Gravity		Solidifying Point		Melting Point		Iodine Value		Butyro-refractometer			Ether-insoluble Bromides	
Per cent	Observer	At 100° C (Water 15) C=1)	Observer	°C	Observer	°C	Observer	Per cent	Observer	At °C	Degrees	Observer	Per cent	Observer
				Titer Test										
93·5	Lewko-witsch	0·8922	Archbutt	22·9-23·9	Lewko-witsch	27	Jean	130·3-132	Schweitzer and Lungwitz	40	43·3	Liver-seger	27·77	Lewko-witsch
						14-15 16·2 18	Schweitzer and Lungwitz						27·81	T-suji-moto
								Liquid Fatty Acids						
								141·7	Clapham [3]					

1 Filtered whale oil of best quality.   2 Oil from *Rhachianectes glaucus*, Cope.   3 Determined in the author's laboratory.

The "water-white" and "pale" brands of whale oil are used as burning oil and in soap-making. The lower qualities are employed for leather-dressing.

Whale oil is also largely used as a "batching oil" for jute, for tempering steel, and as a lubricant for screw cutting machines, for soap-making, and adulterating tallow. As early as 1807 whale oil is said to have been used as a sheep dip.

An emulsion of whale oil with tar and calcium saccharate is used as a protective agent for roofs, walls, etc.[1]

The changes which whale oil undergoes in the preparation of sod oil will be described in Chap. XVI. The change which takes place in whale oil on blowing with air at 100° C. may be gathered from the following tables, due to *Procter and Holmes*[2] :—

Whale Oil

Blown	Specific Gravity	Refractive Index	Iodine Value
Hours			
0	0 933	1 4762	121·0
4	0 936	1·4765	112·0
8	0 937	1 4766	97 5
12	0·948	1·4767	89 0
16	0 949	1·4770	87 0
20	0·950	1·4773	87·0
24	0 950	1·4773	86 0

[1] Cp. Iversen, Danish patent 8420, 1905.
[2] *Journ. Soc. Chem. Ind*, 1905, 1287

[TABLE

Whale Oil, Filtered.[1]

Blown.	No 1.		No 2		No 3.	
	Refractive Index	Dispersion.	Refractive Index	Dispersion	Refractive Index	Dispersion
Hours						
0	1·4740	40·0	1·4740	39·9	1·4732	39·9
3	1·4751	40·1	1·4741	40·0	1·4740	40·0
4	1·4752	40·2	1·4745	40·3	1·4740	40·0
5	1·4753	40·2	1·4747	40·3	1·4750	40·2
6	1·4758	40·3	1·4748	40·4	1·4755	40·3
7	1·4760	40·4	1·4750	40·5	1·4757	40·5
8	1·4762	40·5	1·4754	40·5	1·4759	40·6
9	1·4763	40·5	1·4756	40·5	1·4761	40·6
10	1·4765	40·5	1·4756	40·5	1·4763	40·6
11	1·4768	40·7	1·4757	40·6	1·4768	40·6
12	1·4770	40·7	1·4758	40·6	1·4770	40·7
13	1·4770	40·7	1·4760	40·6	1·4770	40·7
14	1·4771	40·7	1·4760	40·6	1·4771	40·7
15	1·4773	40·7	1·4761	40·7	1·4773	40·7
16	1·4773	40·7	1·4761	40·7	1·4773	40·7
17	1·4773	40·8	1·4762	40·7	1·4773	40·7
18	1·4774	40·8	1·4763	40·7	1·4774	40·7
19	1·4779	40·8	1·4765	40·8	1·4776	40·8
20	1·4780	40·8	1·4765	40·8	1·4776	40·8
21	1·4780	40·8	1·4765	40·8	1·4776	40·8
22	1·4752(?)	40·8	1·4765	40·8	1·4777	40·8
23	1·4782	40·8	1·4765	40·8	1·4777	40·8
24	1·4782	40·8	1·4765	40·8	1·4777	40·8

TURTLE OIL

French—*Huile de tortue.*   German—*Schildkrotenol.*
Italian—*Olio di tartaruga.*

For tables of characteristics see p. 465.

This oil, the characteristics of which are described by *Zdarek* in the following tables, is the body-fat from *Thalassochelys corticata*, Rond. The oil has a yellow colour.

The specimen described by *Sage* appears to have been obtained, according to private information given to the author (by Mr. Ulcoq, Châirman of the Delegates of the Colony of Mauritius at the Franco-British Exhibition, 1908), from turtle belonging to the family *Testudo*

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[1] The samples used for these experiments were supplied by the present author from bulk lots prepared on a large scale.

(Chersidæ). The specimen of oil shown at the Exhibition was of a pale yellow colour, and had a slightly fishy taste.

The specimens examined had the acid value 0·57 (*Zdarek*) and 1·1 (*Sage*).

This oil is now being prepared commercially in Mauritius.

The oil from the Snapping Turtle, *Trionyx sinensis*, Wiegm, is pale yellow, and has a not unpleasant odour ; it deposits some stearine on standing. The following characteristics were determined by *Tsujimoto* [1] :—

Specific gravity at 15 5° C. . . .	0 9229
Saponification value .	195 65
Iodine value .	121·09
Acid value . .	0 45
Refractive index at 20° (Zeiss) .	72·2
	1·4737

The fatty acids melted at 32·8° C. and yielded only 3·53 per cent of insoluble bromides. These bromides gave by the *Carius* method 63·34 per cent of bromine, which points to the presence of linolenic acid. This needs further elucidation.

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[1] Private communication.

Physical and Chemical Characteristics of Turtle Oil

Specific Gravity		Solidifying Point °C	Melting Point °C	Saponification Value	Iodine Value	Reichert-Meissl Value	Refractive Index		Observer
°C 42.5	0.9198	10.0	23-27	209	112	4.6	°C 30	1.4677	Zdarek[1]
25	0.9192	19.18	24-25	211.3	111.0	4.8	50	1.4665	Sage[2]
15	0.9335			193.50	127.4[3]		29	1.4769	Tsujimoto[4]

[1] *Zeits. f. physiol. Chem.*, 1903, 460.
[2] *Chemist and Druggist*, 1906, 691.
[3] Contains 2.51 per cent of oxidised acids.
[4] *Journ. College of Eng. Tokyo Imp. Univ.*, 1906, 178. Green turtle oil from *Chelonia mydas*, Linn.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point °C	Melting Point °C	Iodine Value	Mean Molecular Weight	Ether-Insoluble Brominated Acid Per Cent	Observer
	30.2	119	268	29.45[1]	Zdarek
28.2	31.5				Tsujimoto

[1] Equals 8.98 per cent of clupanodone acid.

<div align="center">DUGONG OIL, MANATEE OIL</div>

French—*Huile du dugong, Huile de lamantin.* German—*Dugongol.*
Italian—*Olio di vacca marina.*

This oil is obtained from the blubber of the sea-cow (*Halicore
australis* and *Halicore indicus*), a herbivorous mammal living near the
shores of the Indian Archipelago, in the Persian Gulf, and in the Red
Sea. In the Indian Ocean the dugong is met with in large herds,
the animals reaching there a length of 5·5 to 6 metres, whereas the
dugong occurring near Australia only reaches a length of 3·6 to 4·25
metres.

<div align="center">*Physical and Chemical Characteristics of Dugong Oil*</div>

Specific Gravity	Saponification Value.	Iodine Value	Reichert Value	Refractive Index. Butyro-refractometer	
At 60° F	Mgrms KOH.	Per cent	cc ¹⁄₁₀ norm KOH	" Degrees "	Observer
0·9203	197·5	66·6	2·5	60·3 at 25° C	Mann [1]
				52·0 at 40° C	Liversege [2]

The specimen of dugong oil examined by *Mann* [1] is stated to contain
3·74 per cent of unsaponifiable matter, and 2·39 per cent of free fatty
acids; that examined by *Liversege* [2] had the acid value 5 and yielded
0·9 per cent of unsaponifiable matter. Its optical rotation is stated to
be −0·1° in a 200 mm. tube. The refraction of the insoluble fatty
acids in the butyro-refractometer at 40° C. was 37·7 " degrees." The
oil is said to have a high medicinal value, but its comparative scarcity
precludes its use.

The dugong oil from the Indian species serves the same purposes
as cod oil and whale oil. The oil from the Australian species is used as
a burning oil.

<div align="center">DOLPHIN OIL, BLACKFISH OIL</div>

<div align="center">French—*Huile de dauphin.* German—*Delphintran.*
Italian—*Olio di delfino.*</div>

For table of characteristics see p. 468.

Dolphin oil, from the blubber of the blackfish (bottlenose dolphin),
Delphinus globiceps, Lam., forms an intermediate link between whale oil
(consisting nearly wholly of glycerides) and sperm oil (a true wax).

[1] *Journ. Soc. Chem. Ind.*, 1903, 1357.   [2] *Analyst*, 1904, 211.

Hooper [1] examined the oil from the gangetic dolphin, *Platanista gangetica* (local name, Susu oil, Sehu oil), and determined the following characteristics :—

Oil—

Specific gravity at 50° C.	.	.	.	0 921
Saponification value	.	.	.	198 8
Iodine value	.	.	.	106 9
Reichert-Meissl value	.	.	.	0 71
Acid value .	.	.	.	21 36

Fatty Acids—

Insoluble fatty acids + unsaponifiable, per cent	.	.	94
Melting point ° C.	.	.	.	25 5
Neutralisation value	.	.	.	205
Iodine value	.	.	.	116 5

No spermaceti could be detected.

The oil obtained from the blubber is kept separate from that obtained from the cavities in the head and from the jaw of the blackfish. *Dolphin body oil* and *dolphin jaw oil* are, therefore, described separately.

*Body Oil.—*The yield of oil from the *blubber* of a dolphin averages from one-sixth to four barrels of 31·5 gallons capacity.

This oil is of a pale yellow colour. On standing it deposits spermaceti (cetyl palmitate) [*Chevreul*]. *Bull* [2] found amongst the liquid fatty acids 14·3 per cent of an acid having the iodine value 285·5, and the neutralisation value 313 2. The oil is remarkable on account of the notable amount of glycerides of volatile fatty acids it contains, a characteristic which it shares with porpoise oil. Hence the amount of insoluble fatty acids + unsaponifiable is only 93 07 per cent (*Moore*).

Bull isolated from a specimen of body oil 2 01 per cent of unsaponifiable matter.

Jaw Oil " Melon oil." [3]—The proportion of glycerides of volatile acids in the jaw oil, *i.e.* the oil from the soft blubber contained in the head and jaw of the blackfish, is larger than in the body oil.

The jaw oil (as also porpoise jaw oil and brown fish oil), is distinguished from all other vegetable and animal oils by the extraordinarily high amount of volatile acids it contains. Hence the proportion of insoluble fatty acids (+ unsaponifiable matter) is only 66·28 per cent (*Moore*).

The jaw oil has a straw-yellow colour and a not unpleasant smell. It is used for lubricating fine machinery, such as watches and typewriting machines.

[1] *Annual Report*, Indian Museum, 1908-1911.
[2] *Chem. Zeit.*, 1899, 1044.
[3] Cp. Archbutt and Deeley, *Lubrication and Lubricants*, p 115.

Physical and Chemical Characteristics of Dolphin Oil

	Specific Gravity		Solidifying Point		Saponification Value		Iodine Value		Reichert Value.		Refractive Index.			
	At °C	Observer.	°C	Observer	Mgrms KOH	Observer	Per cent	Observer	c.c. 1/10 norm KOH	Observer	At °C		Observer	
Body oil	15 0·9256	Bull	Deposits sperma-ceti from 5 to −3	Chevreul	197·3 203·4	Moore Bull	99·5 126·9	Moore Bull	5·6	Moore	15 20	1·4708 1·4682	Utz ..	
												Butyro-refractometer.		
											At °C	Degrees	Observer	
Jaw oil					290	Moore	32·8	Moore	65·92	Moore	15 20	67·7 63·6	Utz	

Tsujimoto[1] examined the oil from *Delphinus longirostris* Gray (Japanese name, Mairuka). He differentiates the oil into three kinds:—

I. *Head oil,* a light yellow liquid yielding only a small quantity of ether insoluble bromides.

II. *Body oil* obtained by boiling, and body oil obtained by roasting, both of which yield considerable quantities of ether insoluble bromides.

III. *Refined head oil* obtained by cooling a crude oil to −12° and removing the stearine.

He gives the following table of characteristics :—

	Oil from Head	Oil from Body		Refined Head Oil
		Boiling Process	Roasting Process.	
Specific gravity	0·9249	0·9286	0·9307	0·9259
Saponification value	279·78	217·22	230·35	277·70
Iodine value	24·48	125·25	114·35	25·67
Reichert-Meissl value	112·31	30·40	44·39	..
Refractive index at 20°	1·4524	1·4717	1·4695	1·4517
Butyro-refractometer	40·0	69·0	65·5	39·0
Acid value	2·30	11·90	3·97	0·26
Octobromides of fatty acids, per cent		24·75		..

The octobromides contain 71·52 per cent of bromine which seems to show that there is present, in addition to clupanodonic acid, an acid of the formula $C_{16}H_{24}O_2$

PORPOISE OIL

French—*Huile de marsouin.* German—*Meerschweintran, Schweinfischtran.* Italian—*Olio di porco marino.*

For table of characteristics see p. 470.

Porpoise oil is obtained from the brown porpoise, *Delphinus phocæna,* L. In the case of porpoise oil also, we differentiate between *body oil* and *jaw oil.*

Body Oil.—The *body* oil was examined first by *Chevreul,* who discovered in it " valerie " acid, named by him " acide phocénique." On account of its somewhat high proportion of unsaponifiable matter, this oil appears to form an intermediate link between the blubber oils and the liquid waxes.

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[1] *Chem. Revue,* 1913, 72.

Physical and Chemical Characteristics of Porpoise Oil

	Specific Gravity			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.		Refractive Index. Butyro-refractometer		
	°C.		Observer.	°C	Observer	Mgrms KOH	Observer	Per cent	Observer	c.c. n/10 KOH	Observer.	°C.	"degrees"	Observer
Body oil	15	0.9258	Bull	−16	Chevreul	195	Bull	119.4	Bull	23.45 [1]	Steenbuch [2]	25	54.8	Thomson
	15	0.926	Thomson and Dunlop			256.6 [3]	Thomson and Dunlop	85.3	Thomson and Dunlop	40.7 [3]	Thomson and Dunlop	40	46.3	son and Dunlop
	16	0.987	Chevreul											
Jaw oil, skimmed and strained	15	0.9258	Bull			253.7 272.3 269.3	Moore [4] Bull	49.6 30.9 21.5	Moore [4] Bull	47.77 56.0 65.8 [4]	Moore [4] „ Steenbuch			
Jaw oil, not skimmed nor strained						143.9 (?)	Moore	76.8 (?), Moore		2.08 (?), Moore				

Insoluble fatty acids—un-saponifiable, 91·04 per cent. Neutralisation value of insoluble fatty acids, 203 (Hart [5])

[1] Reichert-Meissl value, 46·9 and 31·6 and Reichert-Wollny value 81·4, halved for the sake of comparison.
[2] *Zeitschr. f. angew. Chem.*, 1899, 54.
[3] This is undoubtedly a per oil, hence in Vol. I. not registered in list of saponification values.
[4] *Journ. Soc. Chem. Ind.*, 1890, 331.
[5] *Chem. Zeit.*, 1908, 819. The spec. grav. of the oil (evidently body oil) was 0.9302 at 15° C., saponific. val. 222.2, and Maumene test 61° C.

The amount of volatile fatty acids is somewhat high. No further extended inquiry has been made into the composition of the oil (especially into that of the volatile fatty acids) since *Chevreul's* investigation. As the oil can now be obtained easily in commerce a renewed examination is desirable. No doubt the amount of insoluble fatty acids will be found comparatively low. The body oil is pale yellow and resembles the dolphin body oil. It is stated to consist of the glycerides of " valeric," palmitic, stearic, and oleic (and physetoleic ?) acids.

Thomson and Dunlop found a specimen of porpoise body oil to be dextro-rotatory, $[a]j = +0.76^\circ$ (whereas all the liver oils are levo-rotatory). This specimen gave a violet colour in the sulphuric acid test described above as a characteristic test for liver oils (p. 142). It is important to note this, as on the strength of this colour test alone such porpoise oil might be declared as adulterated with liver oil. A specimen of body oil examined by *Bull* contained 3.7 per cent of unsaponifiable matter. *Bull* isolated from a body oil 19.18 per cent of fatty acids having the iodine value 322.5 and the neutralisation value 191.4.

Jaw Oil.—The *jaw* oil simulates the corresponding dolphin oil in its composition.

The jaw oil is easily soluble in alcohol at 70° C.; it is therefore possible to extract it from a mixture of the body and jaw oils. The amount of insoluble fatty acids varies from 61.41 and 72.05 per cent in skimmed and strained jaw oil, to 96.5 per cent in unskimmed and unstrained jaw oil (*Moore*).

In a specimen of porpoise jaw oil *Bull* found 16.4 per cent of unsaponifiable matter, and 21.13 per cent of fatty acids having the iodine value 31.3 and the neutralisation value 367.8. This points to large proportions of " (iso)valeric " acid.

The oil is used, like dolphin oil, for lubricating purposes.

BROWN FISH OIL

French   *Huile de marsouin brun.*   German—*Braunfischol.*
Italian   *Olio di pesce porco.*

For tables of characteristics see p. 172.

This oil is obtained from the brown fish, *Phocæna communis*, belonging to the *Delphinidæ*. The characteristics given in the table refer to the *body* oil. The oil has a pale yellow colour, and possesses a not unpleasant smell. Like porpoise oil it is distinguished by a high proportion of volatile fatty acids. Hence it yields only 85.5 per cent of insoluble fatty acids + unsaponifiable. The acid value of the specimen examined was 1.2.[1]

[1] Schneider and Blumenfeld, *Chem. Zeit.*, 1906, 53.

Physical and Chemical Characteristics of Brown Fish Oil

Specific Gravity at 15° C.	Saponification Value Mgrms. KOH	Iodine Value Per cent.	Reichert-Meissl Value.	Refractive Index. Butyro-refractometer.	
				° C	" Degrees."
0·9334	224·8	111·2	42·1	25	62·7

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable Per cent.	Specific Gravity at 15° C.	Solidifying Point ° C	Neutralisation Value Mgrms. KOH.	Iodine Value Per cent	Acetyl Value Mgrms. KOH
85·5	0·9121	18	207	126	4·55

The oils from marine animals described above were closely examined, on account of the commercial importance they possess. The chemistry of fish oils from fresh-water fish —with the exception of carp oil (p. 423)—has not yet been investigated ; no doubt because these oils have only scientific interest. In view of the fact that the iodine value of carp oil is much lower than that of the marine fish oils, it would appear interesting to examine a larger number of oils prepared from fresh-water fish. The fresh-water eel, containing about 30 per cent of oil (calculated to dry substance) would seem to be a suitable subject for investigation. Possibly a difference might be established between oils from marine fish and oils from fresh-water fish with respect to their iodine value, although the differences in the seal oils from *Phoca vitulina* and *Phoca fœtida* var. *siamensis* (cp. p. 449) do not seem to favour the conjecture, that the oils from sweet-water fish may be generally found to exhibit lower iodine values than the marine animal oils. *König, Thienemann and Limprich*,[1] could not detect phytosterol in the body fat of carp fed on sesamé cake and arachis cake.

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1912 (23), 177

(2) Terrestrial Animal Oils

Hitherto only four oils, viz. sheep's foot, horse's foot, neat's foot oil, and egg oil had been described under this head, and no differentiation was made on account of their origin from quadrupeds and birds respectively, as egg oil seems to resemble the first-named three oils in many respects, such as low iodine value and elaidin test

Oils from other classes of terrestrial animals did not offer sufficient practical interest to induce an examination. Within the last decade, however, the chrysalids, which form a by-product of the silk industry, have been treated on a commercial scale to recover the oil contained in them. The examination of this oil, carried out by the author, showed that, judged by the iodine value alone, it would have to be classed amongst semi-drying oils. A further support is found in that this oil yields a soft buttery elaidin.

Although it may be somewhat premature to subdivide the terrestrial animal oils according to their origin into (1) oils from insects, (2) oils from birds, (3) oils from quadrupeds, this order may be suitably adopted in the following enumeration of these oils.

CHRYSALIS OIL [1]

French—*Huile de chrysalide.*   German—*Chrysalidenol.*
Italian—*Olio di crisalide.*

This oil is obtained by extracting the chrysalids (pupæ) of silkworms (*Bombyx mori*) by means of solvents. A sample extracted in the author's laboratory with ether from a batch of chrysalids (which had also been extracted on a manufacturing scale) yielded 27·2 per cent of a clear, dark yellow oil, from which considerable quantities of crystalline warts separated. The oil had the following characteristics :—

Saponification value	194 0
Iodine value	117·8
Unsaponifiable	4 86 per cent
Acid value	62 8

The annual production of chrysalids in Italy during the period 1899–1908 was about 16,000,000 kgs.

The crude oil prepared on a large scale from the same chrysalids had a dark brown colour, and a distinct smell resembling that of fish oil. By filtering over Florida earth the oil became much clearer.[2] On standing, solid particles separated as amorphous flocks, no doubt due to traces of solvent still adhering to the commercial oil. The commercial oil had the following characteristics :—

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[1] Lewkowitsch, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1906, xii. 659 ; 1907, xiii. 552.

[2] Cp. C. Scerno, Italian patent 385/190/125,423.

Specific gravity at 40° C. (water at 40°= 1) . .	0·9105
Solidifying point	10°·7° C.
Saponification value	190·0
Iodine value	116·3
Unsaponifiable	2·61 per cent
Acid value	27·51
Mean molecular weight of the insoluble fatty acids	281·7
Solidifying point of the insoluble fatty acids .	34·5° C

The considerably lower acid value of the commercial oil is due to the oil in the chrysalids extracted by the author having undergone pronounced hydrolysis (see Vol. I. Chap. I.).

In the elaidin test the oil yields a soft buttery mass.

This oil being the first obtained from insects,[1] it became important to ascertain whether the unsaponifiable matter contained cholesterol like all the oils and fats of animal origin.

A considerable quantity of the unsaponifiable matter was treated with acetic anhydride, whereby 84·67 per cent of the unsaponifiable matter (corresponding to 2·21 per cent of the chrysalis oil) was dissolved, whereas 15·33 per cent (corresponding to 0·40 per cent of the chrysalis oil) remained undissolved. This last substance melted between 54° and 62° C., and is undoubtedly a hydrocarbon.

The substance dissolved in acetic anhydride was recrystallised five times from alcohol, and finally yielded in the fifth crystallisation crystals of the melting point 114° C.

The details are the following :—

Melting point of the 2nd crystallisation					107·5-113° C.
,,	,,	,,	3rd	,,	110-113° C.
,,	,,	,,	4th	,,	112-113·5° C.
,,	,,	,,	5th	,, .	114° C.

Hence the unsaponifiable matter contains cholesterol.

Menozzi and Moreschi,[2] who found " about 10 per cent "[3] of unsaponifiable matter, isolated from this by extraction with 70 per cent alcohol[4] a higher alcohol, melting after repeated crystallisation at 148° C., which they consider differs from the ordinary cholesterol Vol. I. Chap. III.) and has been named "*bombicesterol*." The acetate of this alcohol melted in the impure state at 112-114° C. ; after *one* crystallisation the melting point rose to above 120° C., and after repeated crystallisations to 129° C. On applying *Windaus'* method[5] a small quantity of an acetate melting at 114° C., and a larger quantity

[1] It may, however. be mentioned that *R. Dubois* stated (*Oil, Paint, and Drug Reporter*, 190?, 24) that he had prepared oil from the eggs of locusts.

[2] *Rendiconti della R. Accad. dei Lincei*, 1908, 95.

[3] In a later publication (*Rendiconti della R. Accad. dei Lincei*, 1910, 126) it is admitted that this number is much too high, for on saponifying again *Menozzi and Moreschi* obtained only " about " 2·5 per cent, which is in satisfactory agreement with the figure found by Lewkowitsch.

[4] In the case of the unsaponifiable matter from cantharides fat, which represents a waxy matter, this process did not lead to a satisfactory separation of the cholesterol from the concomitant substances.

[5] *Berichte*, 1906, 518. Cp Lewkowitsch, *Jahrbuch d. Chem.* 1906, xvi. 406.

of an acetate melting at 129° C. were obtained. On passing a pure acetate of the melting point 129° C. through *Windaus'* process, the melting point was unchanged.

Menozzi and Moreschi further isolated from the unsaponifiable matter two hydrocarbons, one melting at 62·5° C., optically inactive, and having the composition $C_{28}H_{58}$, and a second one, which also appears to belong to the saturated series, melting at 11°-12° C.

Duboritz [1] found the iodine value of an Italian chrysalis oil 111·5, and that of an oil obtained from the chrysalids from an Hungarian silk works 138·7. The statement made by *Duboritz* that the oil contains a considerable amount of hydroxylated acids (determined by the faulty method of *Benedikt and Ulzer*) requires confirmation.

Tsujimoto [2] states that chrysalis oil is being prepared in Japan by steaming the powdered dry chrysalids and expressing the mass in a screw or wedge press. A specimen of *pupa* was found to contain

Oil	.	26·6 per cent
Ash	.	. 3·77 ,,
Water	.	. 5·48 ,,

By extracting with petroleum ether boiling below 80° C., an oil was obtained having the following characteristics :—

Oil—

Specific gravity at 15·5° C. .	0·9280
Saponification value	194·12
Iodine value	131·96
Reichert-Meissl value .	3·38
Unsaponifiable matter	1·63
True acetyl value (Lewkowitsch)	19·72
Refractive index at 20° C. .	1·4757

Fatty Acids—

Insoluble fatty acids + unsaponifiable .	94·5 per cent
Specific gravity 100° C. (water at 15·5 1)	0·8513
Melting point .	36·5° C.
Solidifying point .	77-78° C.
Neutralisation value .	199·34
Mean molecular weight .	281·43
Iodine value . .	135·83

The oil had the acid value 18·68. The fatty acids were resolved by the lead-salt-ether method into 75 per cent unsaturated fatty acids (of the iodine value 178·73) and 25 per cent (by difference) of saturated fatty acids (of the melting point 57° C.). Amongst the saturated fatty acids palmitic acid was identified ; stearic acid is probably not present.

[1] *Seifensieder Zeit.*, 1908, 1281.
[2] *Journ. College of Eng. Tokyo Imp. Univ.*, 1908, vol. iv. No. 3. This author refers in a footnote to three papers published in 1905 (*in Japanese*): "Chrysalis Oil Manufacture in the Nagano and Gunma Prefectures," *Report of Indust. Exper. Station*, Tokyo, vol. ii 1905, 473 ; "On Chrysalis Oil," by K. Zasshi ; and " On the Fatty Acids of Chrysalis Oil," by K. Zasshi.

The unsaturated fatty acids consist of oleic, linolenic, and isolinolenic acids. The amount of ether-insoluble bromides—melting at 178° C.—was 11·94 per cent, corresponding to 4·38 per cent of linolenic acid (including isolinolenic acid).

The unsaponifiable matter after recrystallisation from 90 per cent alcohol yielded crystals, melting at 138·5° C. ; after repeated purification they melted at 143·5° C. Their crystalline form is stated to closely resemble that of phytosterol. The acetate obtained from this alcohol by *Bomer's* method melted at 125·5° C. From a second sample of chrysalis oil *Tsujimoto* obtained an alcohol, melting at 137-139° C., the acetate of which melts at 125° C. *Tsujimoto* concludes therefrom that the alcohol in chrysalis oil is phytosterol.

The melting points found by *Lewkowitsch* in five crystallisations (see above) would seem to exclude the possibility of a small amount of hydrocarbon having been persistently retained by the acetate (cp. tables " Melting Points of Cholesteryl Acetate with Paraffin Wax " under " Lard "). The fact that *Menozzi and Moreschi*, after separating off the hydrocarbons carefully and applying *Windaus'* method of separation, did obtain an acetate melting at 114° C. in addition to bombicesterol would seem to prove that what *Tsujimoto* regarded as " phytosterol " was in truth a mixture of cholesterol and bombicesterol. Indeed in a later publication *Menozzi and Moreschi* [1] admit that the unsaponifiable matter contains ordinary (bile) cholesterol.

Since this oil can be obtained without difficulty, it is destined to find an outlet in the soap industry in considerable quantities.

Tsujimoto [2] refines crude chrysalis oil by shaking it with 5 to 10 per cent of 50 per cent sulphuric acid at 100° C. ; subsequently washing and treating with Kambara earth at 130° C. By these means the unpleasant smell is removed.

Tsujimoto states that chrysalis oil is as suitable for hardening as blubber oils, as he has obtained from it solid fats melting at 56° C. and having the iodine value of 35 to 45.

Dorée [3] extracted the entire silk-worms and obtained crystals which " answered the description given by *Menozzi and Moreschi* for bombicesterol," but no definite statement can be made.

CANTHARIDEN OIL [4]

Canthariden oil (from *Lytta vesicaria*) is obtained as a by-product in the manufacture of canthariden. The oil contains about 9 per cent of unsaponifiable matter (of a waxy consistence) from which pure cholesterol could be separated.

[1] *Rendiconti della R. Accad. dei Lincei*, 1910, 126.
[2] *Journ. Chem Ind.*, Tokyo, 1914, 191.
[3] *Biochem. Zeits* , 1909 (4), 84.
[4] Welsch, *Inaug. Dissert.*, Offenbach a/M., 1909.

EGG OIL

French—*Huile de jaune d'œuf.* German—*Eierol.*
Italian—*Olio di novo.*

For table of characteristics see p. 478.

Egg oil is prepared commercially from the yolk of hard-boiled hens' eggs either by pressure or by solvents. Another process consists in separating the yolk of fresh eggs from the white, and beating the yolk until the bulk of the water has evaporated off. The dried mass is then placed in bags and expressed between hot plates. The expressed oil is then filtered. *Paladino and Toso* [1] obtained, by expressing boiled eggs, 25 to 35 per cent of oil; *Kitt*,[2] by using ether as a solvent, 19 per cent only. The ethereal extracts contain, besides egg oil, other substances, notably lecithin; hence the extracted fat is more readily soluble in alcohol than it would appear to be, judging from its composition in the absence of lecithin. *Barbieri* [3] expresses an opinion that no lecithin occurs in egg yolk.

The expressed oil has a yellow colour. The extracted oil, freed by filtration from other ether-soluble substances, was semi-solid and had an orange-yellow colour. The specimen examined by *Kitt* contained 0·2 per cent of lecithin, and 1·5 per cent of cholesterol; its acid value was 1·2. *Cappenberg* states that egg oil contains on an average 3 per cent cholesterol, without adducing any experimental proof.

Egg oil gives the elaidin reaction. The acetyl value 11·9 recorded by *Kitt* does not necessarily point to the presence of hydroxylated fatty acids, since even if the number itself were not open to doubt on account of a faulty method having been applied (cp. Vol. I. Chap. VI.), the high amount of cholesterol in the oil conditions a notable acetyl value.

According to *Paladino* [4] egg oil contains oleic, palmitic, and stearic acids. He also states that formic acid is present; this would, however, seem to require confirmation.

[1] *Analyst*, 1896, 161.   [2] *Chem. Zeit.*, 1897, 303
[3] VII. *International Congress*, Sect. IV A. 2, 62; *Compt. rend.*, 1910, 405
[4] *Biochem Zeits*, 1909, 356.

Physical and Chemical Characteristics of Egg Oil

Specific Gravity		Solidifying Point		Melting Point		Saponification Value		Iodine Value		Reichert-Meissl Value		Refractive Index	
At °C	Observer	°C	Observer	°C	Observer	Mgrms KOH	Observer	Per cent	Observer	c.c. N/10 norm KOH	Observer	At 25°C	Observer
15 0.9144 20 0.9136	Kitt Paladino and Toso	8-10	Paladino and Toso [1]	22-25	Paladino and Toso	199.2 183.2-186.4	Kitt Paladino and Toso	72.1 81.2-81.6	Kitt Paladino and Toso	0.4 0.66	Kitt Spaeth	1.4713	Spaeth
100 (water at 15° =1) 0.881	Spaeth					184.4	Spaeth	68.5	Spaeth			Butyro-refractometer "Degrees" At 25°C — 68.5	Observer Spaeth

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Melting Point		Neutralisation Value		Mean Molecular Weight		Iodine Value	
Per cent	Observer	°C	Observer	Mgrms KOH	Observer		Observer	Per cent	Observer
95.76 [1]	Kitt	30.5-2 34.5-35	Kitt Paladino and Toso Spaeth	194.9	Kitt	288	Kitt	73.25	Kitt
		35	Spaeth					72.6	Spaeth

1 *Analyst*, 1896, 161   2 Capillary tube method

In the commercial determination of the fatty oil in the yolk, the choice of the solvent is by no means immaterial. *Jean*[1] has shown that by extracting one and the same specimen of dried yolk with the following solvents : petroleum ether, ether, carbon bisulphide, carbon tetrachloride, and chloroform, the following respective proportions of oil were obtained : 48·24 per cent, 50·83 per cent, 50·15 per cent, 50·30 per cent, and 57·66 per cent. Another specimen of yolk was extracted successively with the three solvents ; petroleum ether extracted 27·3 per cent of oil ; the extraction with ether then yielded 1·05 per cent ; the subsequent extraction with chloroform furnished an additional 1·37 per cent. *Vignon and Meunieur*[2] recommend chloroform as best suited for the extraction of egg oil, and published the following results :—

	Oil Per cent	Iodine Value of Oil	Unsaponifiable Matter Per cent	Phosphorus calculated to Phosphoric Acid (PO_4H_3) Per cent.
Hen's egg . . .	32·7	52	0·2	2·33
Duck's egg . .	38·9	37·4	2·7	1·91

The saponification value of egg oil extracted from hens' eggs with petroleum ether was 188, and the refractive index at 20·2° C. 1·4655.

Serono and Palazzi extracted the egg yolk with alcohol, and separated the extract into two fractions by means of acetone. The portion soluble in acetone contained a lecithin in which were found oleic and palmitic acids. Smaller quantities of phosphorus compound containing a higher fatty acid were found. The portion soluble in acetone crystallised from the solvent in thin flat blue fluorescent needles, which on exposure to light and air darkened to red brown ; on cooling these crystals cholesterol separated out. By extraction with ether these authors obtained a clear yellow light substance liquid above 15°, and having the specific gravity at 15° 0·9115-0·9527, the saponification value 198·8, iodine value 82·3, acetyl value 3·82. The fatty acids melted at 36-38° C.

Egg oil finds commercial application in the leather industries for "tawing." As regards its employment in tempera painting, cp. German patent 187,211 (*Lupus*).

The terrestrial animal oils from quadrupeds are characterised by low iodine values, lower than those of the non-drying vegetable oils, and by low thermal reactions. They yield solid elaïdins with nitrous acid ; chemically, they are readily differentiated from vegetable oils by means of the phytosteryl acetate test.

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1904, 232.
[2] *Collegium*, 1904, 128, 129.

In addition to the oils obtained from the feet of sheep, horses, and of neat, the liquid fats obtained from lard, horse fat, bone fat, and tallow by pressing would fall under this head. The last-named oils are, however, more suitably described in connection with the raw material from which they are derived.

SHEEP'S FOOT OIL

French—*Huile de pieds de mouton.* German—*Hammelklauenöl, Schafpfotenöl.* Italian—*Olio di piede di montone.*

For table of characteristics see p. 481.

This oil is obtained from sheep's trotters in the manner described under " Neat's foot oil " (see p 484). The sample examined by the author (see table) was prepared in the laboratory.

Sheep's foot oil much resembles neat's foot oil, and is, as a rule, sold as such. This oil has been adopted by *Amagat and Jean* as the standard (*huile type*) for their oleo-refractometer.

Physical and Chemical Characteristics of Sheep's Foot Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumene Test.		Refractive Index. Oleo-refractometer.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees."	Observer.
0·9175	Schaedler	0 to 1·5	Schaedler	194·75[1]	Lewko-witsch	74·74·1[1]	Lewko-witsch	49·5	Jean	0[2]	Jean

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point Titer Test.	
°C.	Observer
20 0·21·1[1]	Lewkowitsch

[1] Specimen prepared in the laboratory.   [2] Sheep's foot oil is the standard oil.

HORSE'S FOOT OIL

French—*Huile de pieds de cheval.*   German—*Pferdefussol.*
Italian—*Olio di piede di cavallo.*

For tables of characteristics see p. 483.

This oil is obtained from horses' feet by boiling them with water.

It is not met with in commerce under its true name, and what is described as horse oil is more or less the liquid portion of horse fat. The horses' feet are usually boiled out together with neats' feet and sheeps' feet, and the resulting oil is indiscriminately sold as neat's foot oil, or at least as " animal " oil.

The specimen rendered in the author's laboratory contained, even after filtering, certain impurities, so that the oil gave several colour reactions which were previously considered as characteristic of marine animal oils (cp. p. 406).   The oil had a high acetyl value, viz. 9·1-10·3, due to changes caused by contact with organic impurities.

Physical and Chemical Characteristics of Horse's Foot Oil

Specific Gravity		Saponification Value		Iodine Value		Maumené Test	
At °C.	Observer	Mgrms. KOH.	Observer.	Per cent	Observer.	°C	Observer.
15	0·9202-0·9205 0·9270	195·0-196·8	Lewkowitsch	73·7-73·9 90·3	Lewkowitsch	38	Jean
	Jean Amthor and Zink				Amthor and Zink		

Insoluble Fatty Acids :—Solidifying Point (Titer Test) 27·1-28·6° C. (*Lewkowitsch*).

NEAT'S FOOT OIL

French—*Huile de pieds de bœuf.*   German—*Ochsenklauenöl,
Rinderklauenol.*   Italian—*Olio di piede di bove.*

For tables of characteristics see pp. 487, 488.

Neat's foot oil (*Oleum bubulum* of the British Pharmacopœia) is
obtained from the feet of cattle by boiling with water.   In this country
the preparation of neat's foot oil is chiefly carried out in small estab-
lishments, in which the by-products and waste material of the slaughter-
houses are worked up ("tripe shops").   The feet are carefully scraped
and washed, the hoofs are cut off, and after the hair has been removed
they are boiled with water in jacketed pans heated by steam, the
water being kept simmering for eight to ten hours.   The oil rises to the
top, and is skimmed off from time to time by means of suitable skimmers.
The oil is then allowed to settle in a warm place, salt being sprinkled
on the top to facilitate the separation of the water.   Finally, the oil
is washed with water, in order to remove any gluey substances, and
filtered.   On cooling some "stearine" is deposited.   In the production
of the best kind of neat's foot oil having a low cold test, the clear oil is
decanted off the "stearine."   Such decanted oil has a cold test of
about 25° to 28° F.   The oil prepared in an establishment standing
under the author's supervision was obtained in this manner.

On a large scale neat's foot oil is obtained as a by-product in the
centres of the meat packing trade, such as in the Chicago stock yards
and in the South American establishments.   There the feet are taken
in their fresh state from the slaughter-houses ("killing-beds"), washed
free from adhering blood and dirt, and sawn by a circular saw into
suitable sizes for further working up.   The chief object of sawing off
the feet is to separate the more costly shin bones from the feet proper,
which latter yield the genuine neat's foot oil.   The fatty matter con-
tained in the shin bones approaches somewhat in consistence horse-
or beef-marrow fat (see below), as the case may be.   When kept separate
it is sold as ",bone oil" (French—*Huile d'os ;* German—*Knochenöl*),
five samples of which examined by *Fahrion* had the following char-
acteristics :—

	I.	II.	III.	IV.	V.
Saponification value ., .	196·1	191·3	190·3	186·7	192·5
Iodine value	74·2	67·4	79·6	79·8	79·0
Acid value	9·0	3·8	2·4	6·2	4·2
Melting point of fatty acids .	34	28-29	14	21	13
Mean molecular weight . .	279·5	280·8	284·7	294·8	279·0

This oil must not be confounded with neat's foot oil, nor with bone fat.
It is, however, customary in America to recover the oil from the shin

bones, together with the neat's foot oil, by boiling the shin bones with the feet. Therefore, American oil has a higher solidifying point than that prepared as described above. The feet are scalded by immersion in boiling water for from 10 to 15 minutes in order to loosen the hoofs, which are removed by a special machine—the "hoof-puller." The boiling out of the hoof must be avoided, as otherwise some colouring matters contained in the hoof would pass into the oil and depreciate its value. It will be readily understood that the greatest speed in the working up of the oil is required, as contact with the putrescible animal matter is apt to set up secondary reactions which lead to the production of a low class oil, containing a high proportion of free fatty acids, and having a dark colour and an unpleasant smell.

The further treatment of the oil is very similar to the one described above. The oil is skimmed off as it rises to the surface, filtered roughly through a fine wire screen, separated from water as far as possible, and then run into vessels provided with close steam coils. Steam is passed through the coils and the water still contained in the oil thereby driven off, whilst at the same time organic impurities (albumen) become coagulated. The dried oil is finally obtained in a perfectly limpid state by filtering.

Neat's foot oil is pale yellow and has a bland taste. Properly prepared oil contains only a very small amount of free fatty acids. On standing the oil deposits "stearine." The glycerides contained in neat's foot oil consist of palmitin, stearin, and olein. Linolin appears to be absent, for *Coste and Shelbourn* found amongst the oxidation products of the liquid acids of neat's foot oil dihydroxystearic acid only. The amount of unsaponifiable matter varies from 0·12 to 0·65 per cent.

Commercial samples of European neat's foot oil, even if not sophisticated with non-animal oils, consist mostly of true neat's foot oil mixed with sheep's foot and horse's foot oils. Frequently tallow oil (" animal oil ") recovered from greases (see Vol. III. Chap. XVI.) is substituted for neat's foot oil. American neat's foot oil mostly contains the oil from the shin bones, which is properly speaking a marrow fat. Hence the solidifying point of American oil lies as a rule above 0° C. American oil is also frequently adulterated with pig's foot grease. The chief determinants in the valuation of the oil are colour, smell, low freezing point, and freedom from free fatty acids.

A comparative examination of the characteristics of neat's foot oil, tallow, and horse oil has been made by *Gill and Rowe*,[1] who give the following figures :—

[1] *Journ. Amer. Chem. Soc.*, 1902, 466.

		Colour, etc.	Specific Gravity. 15° C.	Maumené Test.	Iodine Value.	Titer Test.
Neat's foot oil (1)	.	..	0·915	42·2	72·9	19-20
„ „ (2)		..	0·914	42·2	72·9	18-19
„ „ (3)	.	..	0·919	49·5	67·1	17-18
„ „ (4)	.	.	0·916	42·2	72·1	16
„ „ (5)	.	..	0·916	42·2	66·0	25 5-26·5
Tallow oil (1)	.	.	0·794	35·0	55·8	35-36
„ „ (2)	.		0·794	35·0	56·6	36·5-37 5
„ „ (3)	.	..	0·794	35 0	56 7	34·5-35·5
Horse oils and fats (1)		White brown semi-fluid	0·919	46 0	75 1	32 5-33 5
„ „ „ (2)		Dark brown semi-liquid	0·916	52 1	82 5	30 0-31 0
„ „ „ (3)		Yellow brown liquid	0·922 at 100° C	54·7	86 3	25·0-26 0
„ „ „ (4)		Golden brown nearly solid	0·798	54 2	79 9	30-31
„ „ „ (5)		Very like (4)	0 799	53·5	78·8	34-35

For the purposes of the leather industries a low " cold-test " is of especial importance, as the finished glazed leather becomes coated with a film of " stearine " in cold weather, if neat's foot oil containing a considerable quantity of " stearine " has been used.

The high price of the oil is an incentive to fraud. It is largely adulterated with vegetable oils, such as rape oil and cotton seed oil. Fish oils (blubber oils, whale bone oil) and mineral oils are also used for the same purpose. These adulterants can be easily detected by determining the iodine value. If the amount of added vegetable oils be so small that the indications furnished by the iodine value of the sample, the iodine value of the liquid fatty acids, the saponification value (rape oil), and other chemical or physical tests, do not lead to decisive results, then their presence can be unmistakably ascertained by the phytosteryl acetate test. In order to circumvent this test, vaseline oil (paraffin wax) is added.

Fish oils and blubber oils are best detected by the bromide test ; mineral oil is easily determined and identified by examining the " unsaponifiable " matter.

Neat's foot oil is a valuable lubricating oil for clocks, guns, sewing machines, and other delicate machinery. (A specimen of true neat's foot oil required in *Redwood's* viscosimeter at 140° F., 70 seconds ; and at 200° F., 43 seconds.) It is largely used in the leather industry, in which practically the total quantity of neat's foot oil made is consumed as " fat liquoring " for the treatment of hides and skins for the manufacture of the more delicate grades of leather (gloves, etc.). In the preparation of fat liquors the neat's foot oil is emulsified by the addition of castor oil soap.[1]

[1] O. Krahner, *Chem Revue*, 1910, 1303.

[TABLE

Physical and Chemical Characteristics of Neat's Foot Oil

Specific Gravity		Solidifying Point		Saponification Value		Iodine Value	
At ° C.	Observer.	°C	Observer	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0.9152-0.9165 [1] Jean	-3 to -4.5	Lewkowitsch	194.3 [2]	Lewkowitsch	69.3-70.4 [2]	Lewkowitsch
15.5 (water at 15.5=1)	0.9169-0.9174 [0] Coste and Parry	10 [1]	Jean	195.5-197.4 [3]	Coste and Parry	71.1-72.4 [3]	C. and P.
15.5	0.9161 [4] Coste and Shelbourn			196-199 [5]	Holde and Stange	66.76 [5]	H. and S.
18	0.9112 Stürell					67.1-72.9 [1]	Gill and Rowe

Physical and Chemical Characteristics of Neat's Foot Oil—continued

Reichert-Meissl Value		Maumené Test		Refractive Index	
cc. N/10 KOH	Observer	C	Observer	At 20 C	Observer
10.0	C. and S.	47-48.5	Jean	1.4684 [4]	C. and S.
		42.2-49.5 [1]	G. and R		
		55-58 [3]	C. and P.		

		Oleo-refractometer	
		Degrees	Observer
		-3 to -4	Jean
Specific Temperature Reaction		-1 to -3 at 22 C	Pearmain
C	Observer		
87.9-103.1 [1]	Gill and Rowe		

Butyro-refractometer		
C	°Degrees	Observer
20	64.2 [4]	C. and S.

[1] American oil.
[2] Oil rendered in the laboratory, hence still containing stearine, which is removed on a large scale by refrigerating.
[3] Two specimens of oil rendered in the laboratory.   [4] Average of samples rendered in the laboratory.
[5] Means of eleven samples of pure commercial oil.   [6] Freed from stearine.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
Per cent.	Observer.	At 100° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms KOH.	Observer.	Per cent.	Observer.
95·3-95·5 [3]	Coste and Parry	0·8712. 0·8900 [3] (water at 100° C.=1)	Coste and Parry	26·1	Coste and Parry	29·8- 30·8 [1]	Jean	200·6- 201·2	Coste and Parry	61 98·63·26 [1]	Jean
95·2 [4]	Coste and Shelbourn	0·8713- 0·8719 [4]	Coste and Shel- bourn	*Titer Test.* 26·1-26·5 [2] 16-26·5 [1]	Lewkowitsch Gill and Rowe	28·5- 29·2 [3]	Coste and Parry	202·9- 206·3	Coste and Shel- bourn	74·5-75·8 71 0·77 63·6-69 5	Coste and Parry Coste and Shelbourn

[1] American oil. [2] Oil rendered in the laboratory. [3] Two specimens of oil rendered in the laboratory.
[4] Average of samples rendered in the laboratory.

Dunlop (*Analyst*, 1907, 318), obtained from *calves' feet* a white salve-like fat of the iodine value 71·8, and the refraction 59·0 " degrees " at 25° C. in the butyro-refractometer. The oil filtered from this product at 13·3° C. had the iodine value 74·1.

The fatty oil from *Cydnus indicus* (Westw.), an insect known in India through its aromatic odour, had the following characteristics :—

Specific gravity 15·5°	.	.	.	0·9135
Saponification value	.	.	.	19·1
Iodine value	.	.	.	49·1
Insoluble fatty acids + unsaponifiable	.	.	.	94·8

HORSE OIL (see under " Horse Fat ").

LARD OIL (see under " Lard ").

TALLOW OIL (see under " Tallow ").

In France oil prepared from alligators by boiling out comminuted flesh with water is sold under the name of " Jacaré " fat. It is used in admixture with fish oils in the leather industry. The alligators from Madagascar yield a harder fat than the American [1]

[1] *Chem. Revue*, 1906, 87

II. SOLID FATS

1. Vegetable Fats

Vegetable fats are obtained from plants widely distributed over tropical and sub-tropical regions. In the world's markets hitherto only a few have acquired considerable commercial importance. These are palm oil and its kernel oil, and cocoa nut oil ; cacao butter and Japan wax rank next. There is, however, no doubt that in the near future large quantities of vegetable fats will become available for industrial purposes as the conditions of communication and transport (both by land and sea) with the countries of their origin improve. Tropical Africa, especially tropical West Africa (Nigeria, the French Colonies, and the Soudan), the East Indies, the Sunda Islands, and South Sea Islands, the vast regions of tropical South and Central America are bound to furnish in future large quantities of fats. At present the enormous tracts of French Nigeria, of the Soudan, and of Indo-China are being systematically explored for fruits likely to yield vegetable fats.

The vegetable fats are chiefly found accumulated in the seeds. Vegetable tallow of China, however, forms a coating round the seeds ; and in the case of palm oil the fruit flesh contains considerable quantities of fat, which differs in its chemical composition from the fat of the seed (palm kernel). Whilst, therefore, the palm fruit would be analogous to the olive fruit, in that it yields a fruit oil and a kernel oil, there is this characteristic difference that olive kernel oil has practically the same composition as the oil from the pulp of the fruit. Ouara oil and ouara kernel oil simulate palm oil completely.

The members belonging to this class are solid in temperate climates. They present, however, a variety of gradations from the soft, buttery mass of laurel oil to the hard, wax-like Japan tallow. As the hardness of the fats increases approximately in direct proportion to the decrease of glycerides of oleic acid and linolic acid, the iodine value would most aptly determine, in the absence of other more striking chemical characteristics, the order in which the individual fats should be enumerated.

I have, therefore, grouped the vegetable fats in the first instance in the order of their iodine values.

Palm nut oil and cocoa nut oil, however, have been placed together as undoubtedly constituting, with mocaya oil, maripa fat, and similar fats, a well-defined group, differing from all other vegetable fats by containing a considerable amount of glycerides of lower fatty acids. In this respect they resemble to some extent butter fat.

As other natural groups I have branched off the *chaulmoogra oil* group, comprising three oils (belonging to the *Flacourtiaceae*), which occupy an exceptional position on account of the high dextrorotatory

powers they possess; the *myristica group*, characterised by the large proportion of myristin, which the members of this group contain; the *dika fat* group, characterised by the very large proportions of laurin (larger than in the fats of the *cocoa nut oil* group) contained in dika fat, tangkallak fat, caÿ-cay fat, and kusa fat.

Further groups are formed by classifying the oils relating to laurel oil, palm oil, and cacao butter. The fats relating to the cacao butter group are characterised by the large proportion of glycerides of stearic acid which they contain.

Chaulmoogra Oil Group

(a) CHAULMOOGRA OIL [1]

French—*Huile de chaulmougra (chalmougré)*. German—*Chaulmugraol*. Italian—*Olio di chaulmugra*.

For tables of characteristics see p. 492.

Chaulmoogra oil is obtained from the seeds of *Taraktogenos Kurzii*, King; *Hydnocarpus Kurzii*, Warb.; and *Hydnocarpus heterophyllus*, Kurz,[2] a tree indigenous to Burmah and Assam. The amount available in the Shwegyin division of Burmah is estimated at about 10,000 lbs.[3] The seeds contain a hydrolytic enzyme, so that a high acid value of an expressed oil[4] must be explained by hydrolysis having taken place whilst the seeds were crushed (cp. Vol. I. Chap. II.). On bruising the seeds this enzyme causes a small quantity of hydrocyanic acid to be generated[5] from a cyanogenetic glucoside contained in the seed. From old seeds no hydrocyanic acid is evolved, the cyanogen compound evidently becoming decomposed in the stored seeds.

In the older literature chaulmoogra oil has been confounded with gynocardia oil, owing to the fact that the seeds of *Taraktogenos* and *Gynocardia* are very similar in appearance. The researches of *Power* and his collaborators have finally cleared up the difficulties surrounding the identity of chaulmoogra, hydnocarpus, lukrabo, and gynocardia seeds[6] (For the older literature cp. third edition of this work, p. 694 and *D. Hooper*, "Agricultural Ledger," 1905, No. 5).

At the ordinary temperature chaulmoogra fat is of buttery consistence; it has a faintly yellow colour and a characteristic odour.

The most characteristic physical property of the fat is its high rotatory power; this rotatory power is due to the configuration of its fatty acids. The specific rotation of the oil is $[\alpha]_D^{15} = +52°$ (expressed oil); +51·3 (extracted oil). The specific rotation of the mixed fatty

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[1] Power and Gornall, *Journ. Chem. Soc.*, 1904, 843.

[2] Grimme, *Chem. Revue*, 1911, 102.

[3] Pearson, "Indian Agriculturist."

[4] Indeed, a specimen thus obtained by Power and Gornall had the acid value 23·8.

[5] Cp. also Greshoff, *Pharm. Weekblad*, 42 (1905), 102; and "Linseed Oil," p. 48.

[6] Cp. Pabisch, *Chem. Revue*, 1913, 267.

acids is $[\alpha]_v = +52 \cdot 6°$ (in chloroformic solution). The mixed· fatty acids consist chiefly of homologous acids of the " chaulmoogric series," $C_nH_{2n-4}O_2$; the highest homologue isolated hitherto is chaulmoogric acid. *Power and Barrowcliff* [1] identified also hydnocarpic and palmitic acids. Undecylic (cocinic) acid and hydroxylated acids, stated by *Moss* [2] and *Schindelmeiser* [3] to occur in chaulmoogra oil, are however absent.

On destructively distilling chaulmoogra oil *Lewkowitsch* [4] obtained dextrorotatory hydrocarbons. A purified gynocardia oil is sold under the name of " Antleprol."

Chaulmoogra oil has been chiefly used in the treatment of leprosy and various skin diseases, not only in Indo-China and Siam but also in Europe. It is also prescribed in the incipient stages of tuberculosis. The preparation of methyl- and ethylesters of the mixed fatty acids for medicinal purposes have been patented by *Farbenfabriken, vorm., Fr. Bayer & Co.* [5]

Physical and Chemical Characteristics of Chaulmoogra Oil

Specific Gravity.		Saponification Value	Iodine Value	Observer
At ° C.		Mgrms. KOH.	Per cent.	
...	...	204	90·4-90·9	Lewkowitsch [6]
25 [7]	0·951	213	103·2	Power and Gornall
45 [7]	0·940	...	...	.
25 [8]	0·952	208	104·4	..
40	0·942	.	...	..
		200·3	97·8	Rainsch [9]

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point. ° C.	Melting Point. ° C.	Neutralisation Value.	Iodine Value.	Observer.
Titer Test 39·6	...	...	86	Lewkowitsch [6]
...	44-45 [7]	215	103·2	Power and Gornall

[1] *Journ. Chem. Soc.*, 1905, 896.   [2] *Pharm. Journ.*, 1879.
[3] *Berichte*, 1904, 165 (where the oil is described as gynocardia oil).
[4] *Berichte*, 1907, 4161.
[5] German patent 216,092.   [6] Commercial sample examined in 1890.
[7] Expressed fat.   [8] Extracted fat.   [9] Specific rotation + 56 °.

(b) HYDNOCARPUS OIL [1]

French—*Huile de hydnocarpus.* German—*Hydnocarpusol.*
Italian—*Olio di hydnocarpus.*

For tables of characteristics see p. 494.

Hydnocarpus oil is obtained from the seeds of *Hydnocarpus Wigh-tiana*, Blume. *Grimme* [2] gives as synonymous with *Hydnocarpus Wigh-tiana* the names *H. inebrians*, Wall. ; *Munnicksia Wightiana*, Dennst., a tree indigenous to the western peninsula of India from South Concan to Travancore.   The tree belongs to the same natural order as *Tarakto-genos Kurzii*, King (yielding chaulmoogra oil, p. 491), and *Hydnocarpus anthelmintica*, Pierre (yielding lukrabo oil, p. 495).   The kernels form 70 per cent of the weight of the total seeds and yield under hydraulic pressure 32·4 per cent of fat.   On completely extracting the com-minuted seed with ether 41·2 per cent of fat is obtained.

The fat is a soft solid at the ordinary temperature ; it has a faintly yellow colour and a characteristic odour.   The most characteristic property of the oil is its optical activity ; $[a]_p = +57.7°$ (expressed oil) ; $+56.2°$ (extracted oil).   The rotatory power is due to the presence of hydnocarpic and chaulmoogric acids (Vol. I. Chap. III.).

The expressed oil had the acid value 3·8 ; the extracted oil 7·4. The unsaponifiable matter of the fat was identified as phytosterol.

The mixed fatty acids are optically active ; $[a]_p = +60.4°$ (in chloroform).   From the mixed fatty acids there were isolated, by crystallisation from alcohol, chaulmoogric acid and its lower homologue, hydnocarpic acid.   The acids contained in the alcoholic mother liquor yielded, on distillation under 20 mm. pressure, the following three fractions :—(1) Fraction boiling at 220-225° C.   These acids absorbed 129·1 per cent of iodine, and had $[a]_p = +41.9°$ (in chloroform).   (2) Fraction boiling at 225-230° C.   The acids of this fraction absorbed 131·1 per cent of iodine, and had $[a]_p = +46.6°$ (in chloroform).   (3) Fraction boiling at 230-235° C.   These acids absorbed 140·7 per cent of iodine, and had $[a]_p = +50.4°$ (in chloroform).   The high specific rotatory powers of these fractions point to their containing large proportions of acids belonging to the chaulmoogric series.   On the other hand, their high iodine numbers indicate that they contain an acid or acids belonging to the linolic or linolenic series.   No palmitic acid could be obtained (difference from chaulmoogra oil).

Hydnocarpus oil has been suggested as a substitute for chaulmoogra oil in its pharmaceutical applications, and has been used in the Bombay Presidency with satisfactory results.   The seeds are not yet an article of commerce.   The oil was imported into Germany under the name of " Cardamom oil " or " Marotti fat," and used in the manu-facture of margarine before its toxic properties were known.

[1] Power and Barrowcliff, *Journ. Chem. Soc.*, 1905, 886.
[2] *Chem. Revue*, 1911, 131.

Physical and Chemical Characteristics of Hydnocarpus Oil

Specific Gravity.		Melting Point.	Saponification Value.	Iodine Value.	Refractive Index.	Specific Rotation.
At ° C.		° C.	Mgrms. KOH.	Per cent.	Butyro-Refractometer.	
25	0·958	22·23	207	101·3 [1]	...	...
...	...	...	...	102·5 [2]	...	...
20	0·955 [3]	22·25	202·7	97·6	81·5	− 79·1 [4]
20	0·958	22·24	204·6	96·8	78·6	− 74·8 [5]
...	...	...	203·7-205·3	93·94·7 [6]	70·4-71·3	+58·8 to +64·5 [7]
...	...	...	203·5-208·1	88·5-94 [8]	69·7-71·1	+54·0 to +58·0

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Melting Point.	Neutralisation Value.	Iodine Value.
° C.	Mgrms. KOH	Per cent
41-44	214·0	106·3

The mixed fatty acids of marotti oil consist of 61·63 per cent of saturated fatty acids and 37·98 per cent of unsaturated fatty acids. The saturated fatty acids melted at 36·41° C., and had the mean molecular weight 272·1. The unsaturated fatty acids melted at 30-31° C., and had the mean molecular weight 279.[9]

A specimen of fat from *Hydnocarpus alpina* represented a yellowish butter-like substance, and had the saponification value 209·0 and the iodine value 84·5. The rotation was $[\alpha]_k^{21} = +49$.[10]

The poisonous properties of these oils are probably due to the internal configuration of the fatty acids, and not to an extraneous toxic substance, as after repeated purification the fat still retains its poisonous properties.

Wolff and Koldewijn [11] give the following characteristics :—

[1] Expressed oil.   [2] Extracted oil.

[3] Grimme, *Chem. Revue*, 1911, 132.

[4] Cardamom oil.   [5] Marotti fat.

[6] Crude cardamom oil.

[7] Reusch, *Chem. Zeit.*, 1911, 77.

[8] Refined cardamom oil.

[9] Knorr, *Seifensieder Zeit.*, 1912, 436.

[10] Lendrich, Koch, and Schwarz, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1911, 22, 441.

[11] *Pharm. Weekblad*, 1912, 1049.

Specific gravity at 100° C.	.	.	.	0·898
Solidifying point	.	.	.	22·5
Melting point .	.	.	:	22·26
Saponification value .			.	207
Iodine value			.	84
Acid value		.	.	0·35
Refractive index at 40° C.	.			1·4709
[a],	.	.	.	⊦49·5

(c) LUKRABO OIL [1]

French—*Huile de lukrabo.*   German—*Lukrabool.*
Italian—*Olio di lukrabo.*

For tables of characteristics see pp. 495-6.

Lukrabo oil is the fat obtained from *Hydnocarpus anthelmintica*, Pierre, a tree indigenous to Siam, northern Cochin China, and Camboja.[2] The tree belongs to the same natural order as *Taraktogenos Kurzii*, King (yielding chaulmoogra oil, p. 491), and *Hydnocarpus Wightiana*, Blume (yielding hydnocarpus oil, p. 493). The seeds are exported to China under the name of "Lukrabo" ("krebao" seed of Camboja ; Annamite, "Chung-bao," "Chumbao" ; Chinese "Dai-phongtu"). The kernels form 31·2 per cent of the total seeds. On subjecting the seeds to hydraulic pressure an amount of fat equivalent to 16·3 per cent of the entire seeds was obtained. By complete extraction with ether the amount of fat rose to 17·6 per cent. This fat is, at the ordinary temperature, a nearly white solid, having the same characteristic odour as chaulmoogra oil and hydnocarpus oil. Like the two latter fats, it is optically active. *Power and Barrowcliff* found $[a]_n = +42·5°$ for the expressed oil, and $+51°$ for the extracted oil (in chloroform). The expressed oil had the acid value 7·5, and the extracted oil 8·1.

The mixed fatty acids form a hard white solid ; their specific rotation is $[a]_n = +53·6°$ (in chloroform). Amongst the acids were identified chaulmoogric acid, hydnocarpic acid, and palmitic acid. The presence of oleic acid was also ascertained.

Physical and Chemical Characteristics of Lukrabo Oil

Specific Gravity		Melting Point	Saponification Value	Iodine Value,
° C.		° C.	Mgrms. KOH	Per cent.
25	0·953	24·25°[3]	212	86·4
25	0·952	23·24°[4]	208	82·5

[1] Power and Barrowcliff, *Journ. Chem. Soc.*, 1905, 886.
[2] Cp. Heckel, *Les Graines grasses nouvelles ou peu connues des Colonies françaises,* Paris, 1902, p. 122.
[3] Expressed oil.   [4] Extracted oil.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Melting Point.	Neutralisation Value.	Iodine Value.
° C.	Mgrms. KOH.	Per cent.
42·43	202·5	87·8

GORLEY SEED OIL

Two samples of this seed identified as " *Onchoba echinata* " from Sierra Leone were found to contain about 47 per cent of solid fat which consisted of a mixture of glycerides of chaulmoogric acid and a small proportion of glycerides of liquid fatty acids.[1]

Specific gravity at 15·5° C.	0·898
Saponification value	192·4
Iodine value	99·7
Acid value	4·5
Unsaponifiable matter	1·5
$[a]_p^{17}$	+48·8

The fatty acids had an iodine value of 105·1 and $[a]_p^{18}$ +52·5°.

PITJOENG OIL, SAMAUN OIL

This oil is obtained from the seeds of *Pangium edule*, Reinw., *Hydnocarpus edulis*, Petm., a tree indigenous to the Malayan Archipelago. The seeds contain 50 per cent of a fatty oil having the following characteristics :—

Specific gravity	0·937
Saponification value	178-183
Iodine value	89·94
Titer test of fatty acids	44·4

The seeds contain a cyanogenetic glycoside of which some passes into the oil when it is prepared by the natives, and is only removed by prolonged boiling. The oil prepared in a very primitive fashion by the natives of Java, by heating the dry seeds and passing the mass between boards, is used as an edible oil.[2]

[1] Goulding and Akers, *Chem. Soc. Proc.*, 1913, 197.
[2] Wijs, *Chem. Revue*, 1911, 158.

PARKIA OIL

French—*Huile de Parkia.* German—*Parkiaol.*
Italian—*Olio di Parkia.*

This fat is obtained from the seeds of *Parkia africana,* R. Br.[1]
(Family, *Mimosaceae*). A specimen of seeds obtained from Togo[2]
(West Africa), showed that they contained 16 per cent of fat and 29
per cent of proteids. The seed kernels yielded 22 per cent of fat and
42 per cent of crude proteids. The fruit pulp of *Parkia biglobosa,*
Benth (African locust), a large tree about 50 ft. in height, is used by
the natives of tropical Africa as a food. The pulp is known locally as
" Netté meal." [1]

The oil obtained from the seeds by extracting with petroleum ether
has a golden yellow colour, and is tasteless and odourless ; at the
ordinary temperature it is semi-liquid to solid. The following char-
acteristics have been ascertained in a specimen having the acid value
2·5 : —

Saponification value				.	184·5
Iodine value	.	.	.	.	91·6
Reichert-Meissl value	.	.	.	.	0·6
Refraction in Zeiss Butyro-refractometer—					
at 25°	.	.	.	.	67·2 " degrees "
at 40°	.	.	.	.	58·8 "
Insoluble fatty acids + unsaponifiable	.	.		95·5 per cent

The kernels are used by the natives of the Soudan in the preparation
of the " Daua-Daua " cakes, which are used as a condiment, and also as
food. The " Daua-Daua " cakes (" Daua-Daua cheese ") are largely
sold as an article of commerce in the Soudan markets. The roasted
seeds are known as " Soudan coffee."

PONGAM OIL [3]

French—*Huile de pongam; huile de Hongay.* German—*Pongamol.*
Italian—*Olio di pongam.*

For table of characteristics see p. 498.

This oil is obtained from pongam beans, the fruits of *Pongamia
glabra,* Vent. (*Dahlbergia arborea,* Willd. ; *Gadelupa arborea,* Roxb.,[4]
Gadelupa indica, Lam., *Gadelupa pinnata,* L., *Caju gadelupa,* Rumph.),
a tall tree growing all over East India from the Central and Eastern
Himalayas to Ceylon and Malacca. The tree occurs also in the Malayan
Archipelago, North of Australia, the Pacific Islands, and the Seychelles.

[1] A. Goris and L. Crété, *Compt. rend.,* 1908 (146), 187.
[2] H. Fincke, *Zeits. f. Unters. d. Nahrgs- u. Genvssm ,* 1907 (xiv.), 512.
[3] Lewkowitsch, *Analyst,* 1903, 342.
[4] The pongam seeds must not be confounded with the seeds of *Dahlbergia sissco.*

Physical and Chemical Characteristics of Pongam Oil

Specific Gravity at °C.	Solidifying Point °C.	Melting Point °C.	Saponification Value.	Iodine Value.	Acid Value.	Refractive Index. Butyro Refracto-meter "Degrees."		Unsaponifiable Matter.	Observer.
						At °C.			
15 (water at 15°=1) 0·93693 [1]	...	...	...	...	...	...	...	...	Lewkowitsch
40 (water at 40°=1) 0·9240 [1]	...	...	183·1 [1]	89·4 [1]	...	40	70 [1]	...	...
40 0·9352 [2]	...	...	178·2	94·0 [2]	...	40	78 [2]	...	Grimme [4]
30° 0·9289	±10	+2·0	185·1	77·3	42·28	25°	1·4770 [3]	8·16	

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids	Unsaponifiable.	Solidifying Point. Titer Test. °C.	Melting Point °C.	Neutralisation Value.	Iodine Value.	Refractive Index. At °C.	Mean Molecular Weight	Observer.
...	...	44·4	...	...	...	...	...	Lewkowitsch
91·18	42·5	...	43·8	180·1	78·8	50 1·4637	308·7	Grimme [4]

[1] Specimen obtained from India. [2] Extracted in the laboratory with ether. [3] Refractive Index.
[4] *Chem. Revue*, 1910, 233.

The oil is known under the following native names :—Kanooga-manoo, Kanoogoo, Kanùga-Karra, Kanuga-Chettu, Kanji ; it is also known as Korung oil and Kagoo oil, and in Malabar as Ung.

According to *Lépine*[1] the seeds yield 27 per cent of a yellow oil, of the specific gravity 0·945, solidifying at 8° C.[2] The authors of the *Pharmacographia Indica* state[3] that the oil (called Houge oil in Mysore) expressed from fresh seeds was thick, of a light orange brown colour, and bitter taste (perhaps due to the presence of resinous matter or of an alkaloid). The specific gravity at 18° C. was 0·9458. It yielded 93·3 per cent of fatty acids, melting at about 30° C.

By extracting pongam beans with ether the author obtained 33·7 per cent of a buttery mass of a dirty-yellowish colour, and he was enabled to examine, side by side with the oil extracted from the seeds, a native specimen of oil obtained from India. This specimen contained 0·5 per cent of free fatty acids (in terms of oleic), and 6·9 per cent of unsaponifiable matter. The sample prepared in the author's laboratory contained 3·05 per cent of free fatty acids, and 9·22 per cent of unsaponifiable matter.

The oil is used in India for medicinal and illuminating purposes. As it can be obtained in large quantities, it should find technical application in the soap and candle industries.

LAUREL OIL, BAYBERRY OIL

French—*Huile de laurier.* German—*Lorbeerfett.*
Italian—*Burro di lauro, Olio di lauro.*

For tables of characteristics see pp. 501, 502.

Laurel oil[4] is obtained from the berries of the laurel tree, *Laurus nobilis*, L., either by pressing the pounded berries, or by boiling them with water. The berries contain from 24 to 30 per cent of fat. Laurel oil has a green colour. At the ordinary temperature it has a buttery consistence ; its taste and aromatic odour are characteristic.

Laurel oil is completely soluble in boiling alcohol ; on cooling, crystals of trilaurin separate. Judging from the high iodine value, laurel oil must contain considerable quantities of olein (and perhaps also less saturated glycerides) ; hence the statement occurring in the older literature on this oil, viz. that the chief constituent of laurel oil is trilaurin must be considered as erroneous. The quantity of laurin cannot be very high, as is evidenced by the characteristic numbers given in the tables. The presence of laurin is, however, definitively

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[1] *Pharm. Journ.* (3) xl. 16.

[2] Cp. Heckel, *Les Graines grasses nouvelles ou peu connues des colonies françaises*, Paris, p. 86.

[3] See Watt's *Dictionary of the Economic Products of India*, VI. i. p. 322.

[4] Laurel oil must not be confounded with the oil from the seeds of *Calophyllum inophyllum* (see table facing p. 369), specific gravity, 0·9815 at 16° C. ; saponification value, 196·4 ; melting point of insoluble fatty acids, 37·6° C. Nor should laurel oil be confounded with Indian laurel oil (described p. 238), from the fruits of *Laurus indica*.

proved by the following facts :—On distilling laurel oil in *vacuo*, *Krafft* obtained trilaurin in the distillate. *Matthes and Sander* found the proportion of insoluble fatty acids (determined by *Hehner's* method) 85·8 per cent after deducting 1 per cent of unsaponifiable matter.

The titration number of the insoluble volatile acids was 2·8, but this would, of course, not prove the presence of lauric acid (see Vol. I. Chap. VIII.), as even myristic acid passes over with the water vapours. *Allen* found also small quantities of volatile acids (acetic). A specimen examined by the author (see table of characteristics) had the acid value 26·3, and one examined by *Matthes and Sander*, 9·4.

The unsaponifiable matter of laurel oil consists, according to *H. Matthes and H. Sander*,[1] of melissyl alcohol, phytosterol (melting at 132-133° C.), a hydrocarbon "laurane," $C_{20}H_{42}$ (crystallising from alcohol in fine needles melting at 69° C.), and an oily substance of brown colour having an ethereal odour, the iodine value 191·95 and n_D at 40° C. = 1·5018. The exceedingly small amount of this oil cannot appreciably affect the iodine value of the oil and the opinion of *Matthes and Sander* that the high iodine value of laurel oil is due to the high iodine absorption of the unsaponifiable matter cannot be admitted as correct. The *true acetyl value* of the oil was found by *Matthes and Sander* to be 5·1 ; this figure is largely due to the presence of higher alcohols in the unsaponifiable matter. The *apparent acetyl value* was 15·3 for the oil having an acid value 9·4.

The numbers given in the table of characteristics are somewhat widely divergent. This must be due to the fact that crude laurel oils contain varying amounts of a volatile oil. In order to separate the latter from the fatty oil *Fabris and Settimj*[2] digested crude laurel oil (the characteristics of which are given in the table, p. 501), at a temperature of 0° C. with 95 per cent alcohol, filtered, and washed the undissolved portion with 95 per cent alcohol at a temperature of 0° C. until nothing more was dissolved by the alcohol.

The fat which was insoluble in alcohol had the consistence of tallow, and was colourless and odourless, whereas the (smaller) portion dissolved by alcohol was an oily liquid of a dark green colour and very intense odour. The characteristics of the two portions were as follows :—

	Fat insoluble in Alcohol at 0° C.	Oil soluble in Alcohol at 0° C.
Solidifying point	26-28° C.	...
Melting point	40-50° C.	...
Saponification value . . .	206·5	186·6
Iodine value	65·6	124·1
Insoluble fatty acids + unsaponifiable .	90·0 per cent	...
Butyro-refractometer "degrees" at 40° C. .	53	85

[1] *Arch. d. Pharm.*, 1908 (246), 165.
[2] *Atti del VI. Congresso internazionale di chimica applicata*, Roma, 1907, v. 753.

Physical and Chemical Characteristics of Laurel Oil

Specific Gravity		Solidifying Point		Melting Point		Saponification Value	
°C	Observer.	°C	Observer.	°C	Observer.	Mgrms. KOH.	Observer.
15	Cloéz	24	Villon	23·86	Villon	197·5	Fabris and Settimj
15	Fabris and Settimj	24·25	Fabris and Settimj	32·33	Fabris and Settimj	197·5	De Negri and Fabris
		25	De Negri and Fabris	32·31	De Negri and Fabris	197·7-198·1	Lewkowitsch
						197·210	Morpurgo
						200·9	Matthes and Sander

Specific Gravity values: 0·93317, 9·953

Physical and Chemical Characteristics of Laurel Oil —continued

Iodine Value		Reichert-Meissl Value		Butyro-refractometer				Maumené Test	
Per cent.	Observer	c.c. norm KOH.	Observer	"Degrees."	Observer.	Refractive Index	Observer	°C.	Observer.
67·8	De Negri and Fabris	3·2	Matthes and Sander	80 (at 25° C.)	Fabris and Settimj			115·6	Fabris and Settimj
96·4	Fabris and Settimj	5·4	Fabris and Settimj	72 (at 40° C.)	,,	At 40° C	Observer		
80·4-80·5	Lewkowitsch					1·4643	Matthes and Sander		
75·78·4	Wijs								
66·78	Morpurgo								
82·3	Matthes and Sander								

The insoluble fatty acids from the alcohol-insoluble fat gave the following numbers :—

Solidifying point	. 18·19° C.
Melting point	. 23·24° C.
Iodine value	. 64·7
Iodine value of the liquid fatty acids .	. 98·1

The insoluble acids consisted of equal parts of solid and liquid acids (determined by the lead-salt-ether method).

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable		Solidifying Point.		Iodine Value.	
Per cent	Observer	° C.	Observer	Per cent.	Observer.
86·8	Matthes and Sander	Titer Test			•
83·5	Fabris and Settimj	14·3-15·1	Lewkowitsch	81·6-82·0	Lewkowitsch

On shaking laurel oil with twice its volume of alcohol and filtering, a green filtrate is obtained. Hydrochloric acid converts the colour to a yellowish-green which is not changed by ammonia (*Morpurgo*).[1]

Crude laurel oil gives in the *Baudouin* test a colour reaction similar to, although distinct from, that given by sesamé oil. The alcohol-insoluble fat shows the colouration less distinctly, whereas the alcohol-soluble portion gives a very intense colour reaction (*Fabris and Settimj*).

Laurel oil is only used in veterinary practice. It is stated to be adulterated with other fats (lard), coloured green with copper salts. Lard would be detected by the isolation of cholesterol; copper, by incinerating the oil and examining the ash.

CARAPA OIL, CRAB WOOD OIL, ANDIROBA OIL, TOULOUCOUNA OIL

French—*Beurre (huile) de Carapa ; huile de touloucouna.* German—*Carapafett, Tuluciunafett.* Italian—*Olio di Carapa.*

For table of characteristics see p. 505.

This fat is expressed from the seeds of several species of plants belonging to the genus *Carapa* (Meliaceæ) as *Carapa guianensis*, Aubl., *Carapa moluccensis*, Lam., *Carapa procera*, D.C., *Carapa touloucouna*, Guill. et Perr.

The author received from the Imperial Institute a considerable quantity of the seeds of " *Carapa guyanensis.*" There is some confusion with regard to the botanical origin of these Carapa seeds. The seeds

[1] *Giorn. di farm. di Trieste*, 1905, 353.

were sent from Sierra Leone as *Carapa guianensis*, Aubl., apparently
following a mistake in Oliver's *Flora of Tropical Africa*. The species
founded by *Aublet* was, however, *Carapa guianensis*, and this is confined
to the West Indies and South America. It seems, therefore, probable
that the nuts sent from Sierra Leone are derived from *Carapa procera*,
D.C., of which *C. guianensis*, Oliv., and *C. guineensis*, A. Juss., are
synonyms.

A large proportion of the kernels were mouldy, hence in several lots
of nuts, amounting to about 20 lbs. each, the good and bad kernels, as
also the shells, were determined quantitatively, with the following
result :—

Good kernels	.	.	.	35 5 per cent
Bad kernels .	.	.	.	27 ,, ,,
Shells .	.	.	.	37·5 ,, ,,

The sound kernels yielded by extraction with ether 57·26 per cent
of oil.

A large quantity of good kernels were comminuted in the manner
simulating the operations on a large scale, and were pressed in the cold
in a hydraulic press at a pressure of 150 atmospheres. Thus 24 per
cent of cold-pressed oil were obtained. The cold-pressed cakes were
then broken up, comminuted, warmed to 150° F., and again expressed
in the hot press at a pressure of 150 atmospheres. Thus a further
quantity of hot-pressed oil, amounting to 22·7 per cent of the kernels,
was obtained. The total amount of oil recovered from the kernels
amounted to 46·7 per cent, as against the total contents of 57·26 per
cent obtained by extraction with ether.

The oil extracted with ether—the total oil—had the iodine value
75·09.

The cold-pressed and hot-pressed oils were examined separately,
and gave the following characteristics [1] :—

	Cold Pressed	Hot Pressed.
Oil :—		
Specific gravity at 40° C. (water at 40° 1)	0 9179	0·9174
Specific gravity at 15° C. (water at 15·5 1)	0 9272	0 9327
Solidifying point	12° C.	14° C.
Melting point	15·36° C.	15·48° C.
Saponification value . . .	197 1	196·4
Iodine value	75 67	71 25
Reichert-Meissl value . . .	3 53	3 14
Unsaponifiable matter . . .	1·51 per cent	2 04 per cent
Insoluble Fatty Acids :—		
Fatty acids + unsaponifiable . .	95·15 per cent	92·66 per cent
Solidifying point (titer test) . .	35·45° C.	36·15° C.
Neutralisation value . . .	192·4	192 0
Mean molecular weight of the fatty acids .	291·5	292 1

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[1] Lewkowitsch, *Analyst*, 1909, 10.

The insoluble fatty acids consisted of :—

	Cold Pressed.	Hot Pressed.
"Liquid" acids (yielding ether-soluble lead salts)	65·9 per cent	63·46 per cent
"Solid" acids (yielding ether-insoluble lead salts)	34·1 per cent	36·54 per cent
Iodine value of liquid fatty acids . . .	107·4	108 0
Iodine value of solid fatty acids . . .	16·56	17·87
Stearic acid	13·09 per cent	11·24 per cent

In contradistinction to the oil from *Carapa grandiflora*, the present oil does not contain any optically active substance.[1] The oil and the cakes have a very bitter taste, like all the corresponding products of the other Carapa species.

The information given in the literature on carapa oil is of a very indefinite nature. This is caused to a great extent by the conflict of opinions of the several botanists who have given descriptions of the carapa plant. Thus the *Carapa guineensis*, Sweet, or *C. touloucouna*, Guillemin et Perrot, has been described as a separate species, differing from the *C. guianensis*, Aubl., which grows abundantly in Guiana and especially in French Guiana. Several botanists consider the South American and West African species as identical, especially so *Oliver*,[2] who declares the botanical differences, on the strength of which *A. Jussieu, Richard*, and others discriminated two species, as too unimportant to call for such a subdivision. The difference would seem to be based on the subdivision [3] of the carapa plants into (1) *Pentameræ*, with preduncled flowers and parts in fives, and (2) *Tetrameræ*, with sessile flowers and parts in four. In the former are included *C. procera* and *C. surinamensis*, in the latter *C. guianensis* and *C. moluccensis*. *C. guianensis* and *C. touloucouna* are given in the Kew Index as synonyms for *C. procera*, D.C., and according to a communication on this subject received recently at the Imperial Institute from Kew, *C. guianensis* is *C. procera*.[4]

The natives of Guiana prepare the oil by boiling the kernels with water, and placing them in a heap for a few days, when the mass is triturated in a wooden mortar or between stones. The pulp is then exposed to the sun in an inclined position, so that the exuding oil can drain off. A more advanced process is to boil the mass.

A specimen from Trinidad, examined by *Deering*, had the acid value 22·6 ; the melting point of the insoluble fatty acids was 38·9° C. The numbers hitherto published are collated in the table p. 505.

[1] The observations were made by Dr. Pickles in the *Imp. Inst.*
[2] *Flora of Tropical West Africa*, vol. i. p. 336. Cp. Semler, *Die tropische Agrikultur*, vol. ii. p. 451.
[3] Cp. Drabble, *Quarterly Journal Institute of Commercial Research in the Tropics* (Liverpool University), vol. iii No. 6, p. 21.
[4] Lewkowitsch, *Analyst*, 1908, 184.

Physical and Chemical Characteristics of Carapa Oil

Specific Gravity		Solidifying Point		Melting Point		Saponification Value		Iodine Value		Reichert-Meissl Value	
At °C.	Observer.	°C.	Observer.	°C	Observer	Mgrms. KOH	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm KOH.	Observer.
15	0·912	Milhau[1]	26	Hannau[3]	31	Hannau			72·1	Hannan		
15·5	0·9225	Deering[2]					195·6	Deering	65·4	Deering	2·2 5	Deering
40/40	0·9149	Wright					197·2	Wright	67·7	Wright	3·8	Wright[6]
							196·1	,,	58·5	,,	3·6	,,

1 *Corps gras ind.*, 1899, 1.   2 *Journ. Soc. Chem Ind.*, 1898, 1156

3 *Ann. del Lab. delle Gabelle*, 1891–1892, p. 271.   4 Calculated by the author from the bromine value 41.

5 Calculated by the author from Deering's analytical data ; volatile fatty acids equivalent to 0·25 per cent KOH.

6 *Bull. of the Department of Agric.*, 1910. ix. No. 65.

The percentages of insoluble fatty acids + unsaponifiable were found by *Deering and Milliau* to be 93 7 and 95·5 respectively.

Grimme [1] obtained by extraction with ether only 31·54 per cent of oil from the kernels equal to 22·84 per cent of the total seed. *Sprinkmeyer and Diedrichs*,[2] on the other hand, extracted by means of ether 52·9 per cent of oil from an old sample of seed. The oil contained 7·8 per cent of free fatty acids. The figures of these observers are collated in the following table :—

	Grimme Ether Extract.	*Sprinkmeyer and Diedrichs* Ether Extract.		
		I. Crude	II. Crude.	I. Neutralised
Specific gravity at 15·5° C.	0·9238	..	..	..
Solidifying point . .	8·9	..	32·3 [3]	..
Melting point . . .	..	..	37·5 [3]	..
Saponification value . .	201·2	194·90	195·15	194·80
Iodine value . . .	56·8	58·90	58·49	64·9
Acid value . . .	5·3	16·48	75·32	.
Refractive index at 40° .	1·4686	53·0	50·0	51·7
Unsaponifiable, per cent	0·97	..	..	0·40
Reichert-Meissl value .	..	..	2·53	2·30
Insoluble volatile acids .	..	..	0·4	0·5

Château [4] discriminated as two separate oils "Carapa oil" (from *C. guianensis*) and "Touloucouna oil" (*C. touloucouna*). This distinction had been emphasised by *Heckel*.[5] In the following tables the numbers given by him are collated.

	Carapa Seeds.	Touloucouna Seeds.
	Per cent.	Per cent
Shells	24	28·75
Kernels	76	71·25

[1] *Chem. Revue*, 1910, 179.
[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1912, 592.
[3] Polensky's method.
[4] *Les Corps gras industriels*, Paris, 1863, p. 293.
[5] *Les Graines grasses nouvelles ou peu connues des colonies françaises*, Paris, 1902, p. 141.

	Carapa Oil	Touloucouna Oil.
Yield of oil from the total fruit . . .	24 60 per cent	43 46 per cent
Specific gravity at 15° C .		0 932
Maumené test	34° C.	30° C.
Yield of fatty acids by "saponification process"	94 9 per cent	93 27 per cent
Solidifying point of these acids . .	36 2° C	32·65° C.
Yield of fatty acids by distillation process .	86 3 per cent	83 per cent
Solidifying point of these acids .	39 2° C.	39° C
Yield of solid fatty acids by "saponification process"	43 per cent	27 25 per cent
Solidifying point of these acids . .	53° C	51° C.
Yield of solid fatty acids by "distillation process"	49 28 per cent	48 per cent
Solidifying point of these acids .	49° C	48° C.
Yield of glycerin	9·3 per cent	10 58 per cent

These numbers appear to refer to experiments carried out on a manufacturing scale in candle works. The differences shown do not, however, in the author's opinion, establish a definite distinction between the two oils, and in view of the uncertainty attaching to the origin and to the original condition of the fats, especially having regard to the conflict of opinions on the part of expert botanists, the author does not consider that there is sufficient justification for considering "carapa oil" and "touloucouna oil" as two different individuals. Moreover, the name "touloucouna" seems to be, if not a corruption of the name, at least of the same origin as that of *talloconah*, a native name in British Guiana for the carapa tree,[1] known there also as "crab" and "corap."

Dawe (of the Forestry Department) discovered a new species of *Carapa*, which has been named *Carapa grandiflora*, Sprague. The author received a considerable quantity of the nuts from the Imperial Institute, and examined the oil obtained from them.

Oil from Carapa Grandiflora [2]

A large portion of the kernels were mouldy, and in several lots of nuts amounting to about 10 pounds each the good kernels and shells were determined quantitatively with the following result : —

Good kernels 36·3 to 42·1 per cent , bad kernels 25 to 22·3 per cent ; shells 38·7 to 35·6 per cent. The good kernels yielded on extraction with ether 30·26 per cent of oil.

The large quantity at the author's disposal permitted the preparation of cold-pressed oil, hot-pressed oil, and cake on a semi-large scale. For the preparation of the hot-pressed oil good kernels were selected, comminuted in a manner simulating the operations on a large scale, and expressed in the cold in a hydraulic press at a pressure of 150 atmospheres. The amount of cold-pressed oil so obtained was over 10 per cent of the raw material. The cold-pressed cakes were then

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[1] Malonay, *Sketch of the Forestry of West Africa*, p. 296.
[2] Lewkowitsch, *Analyst*, 1908, 186.

broken up comminuted and heated to 150° F. when they were again
expressed in the hot press at a pressure of 150 atmospheres. Thus a
further quantity of hot-pressed oil, amounting to almost double the
quantity obtained by cold expression, was recovered. Quantitative
recovery of the oil was, of course, out of the question, and the cakes
finally obtained, contained much more oil than would be left in a
commercial oil cake.

The cold-pressed oil as also the hot-pressed oil were examined side
by side with the result set out below. The colour of the cold-pressed
oil is almost white with a tinge of pale yellow. At the ordinary tem-
perature it solidifies. The hot-pressed oil is much darker in colour,
and remains solid at the ordinary temperature.

Oil	Cold pressed	Hot pressed
Specific gravity at 40° C. (water at 40 = 1) .	0·9171	0·9215
Specific gravity at 15 5° C. (water at 15·5 = 1)	0·9261	0·9306
Solidifying point .	8° C.	10° C.
Melting point . .	15-23° C.	20-30° C.
Saponification value	198 1	201·8
Iodine value . .	83 7	72·6
Reichert-Meissl value . .	3 75	3·83
Unsaponifiable matter, per cent . .	3·75	1·59

Insoluble Fatty Acids	Cold pressed	Hot pressed.
Fatty acids + unsaponifiable, per cent	94 03	92 93
Solidifying point (Titer test), ° C. .	34 9	38 9
Neutralisation value . .	202·3	202 1
Mean molecular weight of the fatty acids .	277·3	277·1

The insoluble fatty acids consisted of :—

	Cold pressed	Hot pressed
"Liquid" acids (yielding ether-soluble lead salts), per cent	72·82	64·62
"Solid" acids (yielding ether-insoluble lead salts), per cent	26·47	34·93
Iodine value of liquid fatty acids . .	91 71	94·71
Iodine value of solid fatty acids . . .	8·8	9 97
"Solid" acids yielded "stearic acid," melting point 65·6° C, per cent	3 15	6·6

The cold-pressed oil rotated the plane of polarised light 2° 4' to the
left in a 100 mm. tube (the rotation is very likely due to the presence
of a resin).

The oils as also the cake have an intensely bitter taste, which seems
to be characteristic of all the oils derived from the seeds of the *Carapa*

family. Hence the oil is unfit for edible purposes. Carapa oil is used in Brazil, Guiana, the West Coast of Africa, India, and the Moluccas, as an ointment, to protect the natives against the attacks of insects, and for burning purposes. The statement that carapa oil is exported from South America into England and France for soap-making purposes requires confirmation. From notes occurring in the literature on this subject, and from private information given to the author, it appears that seed from *C. touloucouna* was expressed in Marseilles on an experimental scale some time ago, but at present no seeds are being imported into France. The cake so obtained was stated to contain 27·3 per cent of proteids. The commercial value of the kernels must depend upon the use that can be made of the cakes. If the bitter principle in the cakes precludes their use as cattle food, they can only be sold as manure, and their value would then be low.

NUX VOMICA FAT

French—*Huile de noix vomique.* German—*Strychnusol, Brechnussol.* Italian—*Olio di noce vomica.*

For tables of characteristics see p. 510.

This fat is obtained from the seeds of *Strychnos nux vomica*, L., by extraction with ether. The alkaloids strychnine and brucine which form 3·18 per cent of the crude fat (*Schroeder*[1]) are extracted together with the fat; they are removed by washing the crude extract with dilute acid. The yield of fat from the seeds is, according to *Harvey and Wilkie*,[2] about 4 per cent (4·2 per cent (*Schroeder*)).

The export of nux vomica seeds from India is given in the following table :—

	1910.	1911.
	Cwts.	Cwts.
Madras . . .	34,767	39,537
Bengal .	3,878	10,473
Bombay . . .	1,309	1,308

The total yearly production throughout India is estimated at 2000 tons.

The fat is slightly fluorescent in its melted state ; it has a yellowish-brown colour, an unpleasant, but not bitter, taste and a characteristic odour. The fat, prepared as above described, contains a considerable amount of unsaponifiable matter ; 12-12·4 per cent (*Harvey and Wilkie*), 16·93 per cent (*Schroeder*). In agreement herewith the saponification value is low. The solid fatty acids determined in one specimen, amounted to 24·2 per cent, and the liquid acids to 58·4 per cent (*Harvey and Wilkie*). According to *Schroeder* the fat contains 8·6 per cent of solid glycerides (palmitin and arachin) and 74·5 per cent of olein.

[1] *Arch. d. Pharm.*, 1905 (243), 635.   [2] *Journ. Soc. Chem. Ind.*, 1905, 718.

Physical and Chemical Characteristics of Nux Vomica Fat

Specific Gravity		Melting Point	Saponification Value	Iodine Value	Reichert-Wollny Value	Acetyl Value	Observer.
°C		°C	Mgrms KOH	Per cent	c.c. $\frac{N}{10}$ norm KOH		
$\frac{100}{\text{(water }15.5° = 1)}$	0·8638	Softens at 29 Clear at 31·2	168·9-170·6	73·8-79·3	0·7-1·33	11·68	Harvey and Wilke
20	0·8826	Clear at 28	166·2[1]	69·4[1]	1·7	42·23	Schroeder

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable. Per cent	Mean Molecular Weight.	Iodine Value of the Liquid Fatty Acids	Observer.
95·2	281·2	94·0-96·2	Harvey and Wilke
94·9	...	...	Schroeder

[1] Before removal of the alkaloids the saponification value was found to be 160 and the iodine value 61·2.

The unsaponifiable matter of the specimen examined by *Harvey and Wilkie* had the iodine value 89·1, therefore the iodine value of the true fat would be somewhat lower than 73·8. The acetyl value of the unsaponifiable matter was found to be 105·9 ; it had the specific rotation in chloroform solution + 39°. (As phytosterol is lævorotatory there must be present a substance of high dextrorotatory power.) *Heiduschka and Wallenreuter* [1] separated the unsaponifiable matter into two fractions by means of their acetates. To the first, melting at 121° C., they ascribe the formula $C_{40}H_{70}O_2$ The second, which melted at 221° C., they gave the formula $C_{32}H_{54}O_2$. After hydrolysis the melting points were 99° and 186° C. respectively.

BAOBAB OIL—RENIALA OIL—FONY OIL

French *Huile de baobab* (*huile de reniala* ; *huile de fony*).
German—*Baobabol* ; *Affenbrotbaumol*. Italian - *Olio di baobab*

Physical and Chemical Characteristics of Baobab Oil

Source.	Specific Gravity at 15 C.	Solidifying Point F°	Melting Point °C	Saponification Value Mgrms. KOH	Iodine Value	Observer
Adansonia digitata . .	0·915	+ 3 to −3	.	191·7 191·5 190·5 190·5 191·7	. 77·8 76·7 76·7 77·8	Suzzi Bontoux ,, Pelly [4] ,,
	0·915					
Adansonia Grandidieri .	0·9187	13 11·12	21 24·25	56·8 190·9[2] 189·9[3]	55·0[2] 53·9[3]	Millau Bontoux ,,
	0·9190 (20)	13	20·21	192·4	65·66	Thomas and Borry

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Source.	Insoluble Acids + Unsaponifiable Per cent.	Solidifying Point °C	Melting Point C	Neutralisation Value Mgrms KOH.	Iodine Value	Observer.
Adansonia digitata .		34·32	35·5-38·5	197·5	.	Suzzi
	95·8	..		...	...	Bontoux
Adansonia Grandidieri .		43·2	55	..		Millau
	95·5	44·2		. .		Bontoux
	95·5	44·5	51-52	179·0[5]	66-67	Thomas and Borry
				Liquid Fatty Acids		
				97·6		Millau

[1] *Archiv. d. Pharm.*, 1912, 398.   [2] Expressed oil.
[3] Extracted oil.   [4] *Journ. Soc. Chem. Ind.*, 1913, 778.
[5] These had the saponification value 202·5, showing the presence of notable proportions of lactones.

Baobab oil is obtained from the seeds of various trees belonging to the genus *Adansonia*, in especial from *Adansonia digitata*, L., a tree widely distributed over tropical Africa ; *A. Za*,[1] Baillon ; *A. madagascariensis*, Dr. ; *A. Grandidieri*, Baillon, known in Madagascar as *Reniala Fony*; *A. rubrostipa*, Jum. et Perr. ; *A. alba*, Jum. et Perr. ; *A. gregori* (Australia). The bark of the tree yields a material used for paper-making. The shape and the size of the fruits of the different species and their seeds and the proportions of fat contained in them vary considerably. Thus *Balland*[2] obtained from kernels brought from Madagascar 63·2 per cent of a fat melting at 24° C. Seeds obtained by *Suzzi* in Erythrea (Italian East Africa) were smaller and contained much less glycerides. Whereas the seeds examined by *Balland* gave 36·7 per cent of shells, *Suzzi's* specimens yielded only 20 per cent. The whitish pulp contained in the Madagascar seeds yielded by expression 39·02 per cent of fat (*Milliau*[3]). *Suzzi*[4] obtained from the kernels of the Erythrean seeds 32·7 per cent of fat of an oily consistence.

A more complete survey of the difference presented by the various seeds of *Adansonia* species is given in the following table, due to *Bontoux*[5] :—

Source.	100 Seeds weigh (Grms.)	Shells. Per cent.	Kernels. Per cent.	Proportion of Fat in	
				Kernels. Per cent.	Whole Seed. Per cent.
Adansonia digitata (Senegal) .	45·2	59·2	40·8	30·7	12·5
Adansonia Za (Madagascar) .	48·5	52·2	47·8	34·3	16·4
Adansonia madagascariensis (Madagascar) . . .	78·0	44·8	55·2	60·5	34·4
Adansonia Grandidieri (Madagascar)	117·0	32·8	67·2	63·5	42·6

The expressed oil has a golden-yellow colour and a pleasant taste ; the " Fony oil " in especial has a very pleasant nutty taste. The fats extracted with carbon bisulphide have a red colour, which seems to be due to traces of sulphur contained in the solvent, for in the *Halphen* test (see " Cotton Seed Oil," p. 203) all the oils gave a strong colouration, much more intense than that obtained with cotton seed oil.

[1] Cp. A. Jumelle and E. H. Perrier de la Bathie, *Les Matières grasses*, 1909, 1308, 1343, 1509, 1627.

[2] *Journ. Pharm. Chim.*, 1901 (20), 529.

[3] *Compt. rend.*, 1904 (134), 808. *Agriculture pratique des pays chauds*, 1904, p. 658.

[4] *I Semi oleosi e gli oli*, published for the Milan Exhibition, 1906.

[5] Lewkowitsch, *Technologie et analyse chimiques des huiles, graisses et cires*, traduit par E. Bontoux, Paris, vol. ii. 908.

MARGOSA OIL [1]

(VEEPA OIL, VEPPAM FAT, NEEM OIL)

French—*Huile de margosa*; *huile de margosier.*   German—*Margosaöl.*
Italian—*Olio di margosa.*

This oil is obtained from the seeds of *Melia Azadirachta*, L.[2] (*Azadirachta indica*, Juss.), a large tree, 10 to 50 feet in height, growing in the wild or (more often) cultivated state throughout the greater part of India and Burma.

The oil has been described somewhat fully in the *Pharm. Journ.* by *Warden*.[3]

The specimen of fat examined by the author was solid at the ordinary temperature. The titer test of the insoluble fatty acids was 12° C.

Physical and Chemical Characteristics of Margosa Oil

Specific Gravity		Saponification Value	Iodine Value	Reichert-Meissl Value	Refractive Index		Observer
At °C					Butyro-refractometer at 40 C		
						°Degrees	
16 (water at 16 C)	0·91123	196 9	69 6	1 4	52		Lewkowitsch
40 (water at 40 C)	0 9023						

NIAM FAT,[1] MENI OIL, ZAWA OIL.[5]

French—*Beurre de Méné (Meni)*, *graisse de Niam.*   German—*Niamfett.*   Italian—*Grasso di Niam.*

Niam fat is obtained from the fruits of *Lophira alata*, Banks, a tree indigenous to Senegambia, Sierra Leone, and the Egyptian Soudan, and growing profusely along the West Coast of Africa from the Senegal to the Congo. This tree (amongst others) supplies the so-called African oak. Specimens of undecorticated seeds, produced in Sierra Leone, were submitted to the author by the Imperial Institute, together with a sample of oil extracted from the kernels by the natives in the Egyptian Soudan.[6]

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[1] Lewkowitsch, *Analyst*, 1903, 342.
[2] This must not be confounded with *Melia Azedarach*, L.
[3] See Watt's *Dictionary of the Economic Products of India*, vol v p. 211.
[4] Cp. also Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1907, 1265.
[5] Vernacular name in the Egyptian Soudan.
[6] *Bull. Imp. Inst.*, 1912, 226.

Further specimens of Niam fat [1] furnished the following character-
istics :—

Oil—

Specific gravity at 40° C.	.	0·9044	0·9044	0·9019	0·9016
Saponification value	.	181·5	194·6	180·7	183·3
Iodine value .	.	69·8	70·3	72·1	72·5
Reichert-Meissl value	.	0·9	0·9	0·8	0·8
Unsaponifiable matter		0·5	..	..	0·86
Acid value	.	25·9	33·2	47·5	48

Fatty Acids—

Titer test, ° C.	.	49·0	47·0	47·5	48·5

The fruits from Sierra Leone consisted of 61·5 per cent of kernels
and 38·5 per cent of husks. *Heckel* [2] obtained from the fruits from the
Gaboon and the Congo 37 per cent of husks and 63 per cent of kernels.
Ether extracts from the kernels, together with the fat, a black resinous
mass, which separated out from the oil on evaporating off the ether.
This black resinous matter amounted to 0·8 per cent of the weight of
the kernels. The fat freed from the black resinous matter formed
31·19 per cent of the kernels. Therefore the yield of fat from the whole
seeds amounts to 19·18 per cent. It represents, at the ordinary
temperature, a soft buttery mass, melting at 24° C.

The following characteristics of the fat extracted from the kernels,
and also of the fat prepared by the natives of the Egyptian Soudan,
were determined in the author's laboratory :—

	Fat extracted from Kernels	Fat prepared by Natives
Specific gravity at 40° C. (water at 40=1)	0·9105	0·9063
Acid value . . .	18·51	5·78
Saponification value . .	195·6	190·1
Unsaponifiable matter per cent	1·49	1·38
Iodine value . . .	68·4	78·72
Mean molecular weight of the fatty acids . . .	...	283·7
Solidifying point of the fatty acids (Titer test), ° C. .	...	42·5

Edie [3] resolved the insoluble fatty acids by the lead-salt-ether
method into solid acids, having the neutralisation value 195 and the
iodine value 22·5, and liquid fatty acids, having the neutralisation value
196 and the iodine value 134·5. *Pickles and Heyworth* [4] identified
among the solid acids arachidic and palmitic acids, and showed that the
liquid acids contain oleic and linolic acids, linolenic acid being absent.

In West Africa this fat is known as " Niam fat " or " Meni oil."

[1] *Bull. Imp. Inst.,* 1908, 244.
[2] *Les Graines grasses nouvelles ou peu connues des colonies françaises,* Paris, p. 161.
[3] *Quart. Journ. Inst. Comm. Research in Tropics* (Liverpool University), 1907,
2, 124.
[4] *Analyst,* 1911, 494.

It seems preferable to adopt the name Niam fat.[1] The fat has an unpleasant taste, due probably to the small quantity of dissolved resin. Nevertheless, the natives use it for culinary purposes ; it is also used as a hair oil. In the Egyptian Soudan the fat represents nearly always a clear liquid, melting at 10·5° C., having a dark colour and an unpleasant taste.[2]

The seeds of *Lophira procera* (" Kaku ") obtained from the Gold Coast consisted of 25 per cent of shell and 75 per cent of kernels. The kernels yielded 55·3 per cent of a yellowish solid fat similar in character to the fat from *Lophira alata*.[2]

KADAM SEED FAT [3]

French—*Beurre de Kadam.*   German—*Kadamsamenfett.*
Italian—*Burro di semi di Kadam.*

This fat is obtained from the seeds of *Hodgsonia* (*Trichosanthes*) *Kadam*, Miq., a climbing plant belonging to the *Cucurbitaceæ*, and occurring in Padang (Sumatra).

Kadam seed fat is prepared by cutting the fruit into pieces, drying in the sun for a couple of days, and then expressing in bags.

The fat has, at the ordinary temperature, the consistence of butter ; it is yellow, non-drying, and odourless. It consists of 80 per cent of triolein and 20 per cent of tripalmitin.

Specific Gravity.		Melting Point		Saponification Value		Iodine Value	
At 15° C	Observer	° C	Observer	Mgms. KOH	Observer	Per cent	Observer.
0 919	Sack	21	Sack	197 6	Niederstadt [4]	68 96 [5]	Sack [3]
						66 [4]	Niederstadt

MANI OIL

French—*Huile de graines de Mani.*   German—*Maniol.*

The oil is obtained from the kernels of *Symphonia globulifera*, L. fil [6] (*Moronobea coccinea Aublet*), a tree reaching a height of 25 to 35 metres, and occurring in the forests of French Guiana and French Antilles (Guadeloupe). The fruits (with shells) from Guiana contain 32-38 per cent of fatty matter, the kernels alone 62-68 per cent.

[1] Cp. Schweinfurth, *Botan. Ergeb. der ersten Niam-Niam Reise.*
[2] *Gordon Memorial College*, 1908, 413 ; cp. also *Bull. Imp. Inst.*, 1909, 367.
[3] Sack, *De Indische Mercuur*, 1903, 28 (April).
[4] Fat obtained from Brazil.
[5] Calculated by the author from the numbers given in the original paper.
[6] E. Heckel, *Les Matières grasses*, 1909, 1625.

The kernels are ovoid in shape, about 1-2 inches long and $\frac{3}{4}$-1 broad. Their inner portions are mottled yellowish white in the fresh state, but on long standing they become dark. This is caused by a resinous substance which in the fresh kernel is yellow, but becomes oxidised on exposure to the air (owing to the presence of an oxydase and a laccase (?) *Heckel*). The resinous substance can be separated from the fat by alcohol. This resin, which is stated to form 30 per cent of the fat obtained by extraction with carbon bisulphide, does not appear to pass into the fat on extracting the kernels with petroleum ether to any considerable extent, as may be judged from the following numbers obtained by *J. E. Southcombe*.[1] The fat so prepared had a dark reddish colour, an acid value of 10·1, and contained 1·1 per cent of unsaponifiable matter. The following characteristics were determined :—

Oil—

Specific gravity at 99°-100° C.	0 8849
Melting point, ° C.	35
Saponification value	194 6
Iodine value	61 2
Reichert-Meissl value	1 00

Fatty Acids—

Insoluble acids + unsaponifiable	94 3
Solidifying point, ° C.	46
Melting point, ° C.	48-50
Iodine value	64·8

The oil from *Symphonia fasciculata*, Baillon, examined by *Heckel*,[2] yielded insoluble acids + unsaponifiable 95 per cent, and had a melting point 49·7° C. , it also yielded 10·26 per cent of glycerine.

The oil from the seeds of *Symphonia laevis* (yield 35·2 per cent) had an iodine value of 66·7, and was separated by the lead-salt-ether method into 40 per cent of solid and 60 per cent of liquid acids. The seeds of *Symphonia louveli* yielded 40 per cent of fat on extraction with petroleum ether, very similar in its characteristics to the fat from *S. laevis*.[3]

KATIO OIL[4]—KACHAU OIL—KATIAU OIL

Katio oil is obtained from the seeds of *Bassia Mottleyana*,[5] *C. B. Clarke*, a tree belonging to the *Sapotaceæ*, which grows in abundance in the swamps of the Sadong and Saribus districts of Sarawak. A sample of oil prepared by Dyaks gave the following characteristics, which are contrasted with those of the fat extracted from the kernels in the Imperial Institute :—

[1] *Journ. Soc. Chem. Ind* , 1909, 499.
[2] *Chem. Revue*, 1909, 52.
[3] A. Hébert, *Bull. Soc. Chim.*, 1913, 1039.
[4] C. J. Brooks, *Analyst*, 1909, 207.
[5] *Bull. Imp. Inst.*, 1912, 549.

	Native Oil	Native Oil.	Oil extracted in Imperial Institute
Specific gravity at 15 5° C.	0 917	..	..
Solidifying point, ° C.	14	..	.
Saponification value	189 5	191 5	191
Iodine value	63 2	65 0	65
Reichert-Meissl value	..	0 6	0 8
Butyro-refractometer at 40° C	53 4	.	
Insoluble fatty acids + unsaponifiable (per cent)	94·6	96 0	.
Unsaponifiable matter	0.41	..	.
Solidifying point, ° C.	36	36 3	36 4
Melting point, ° C.	37 5	.	.
Iodine value	62 5		.
Mean molecular weight	285		..

The seeds are small, oval, brown in colour, and weigh on an average 0·391 grms. The total seeds contain 40 per cent of oil. The fruit contains inside a thin, crisp, easily removable shell, a kernel yielding 47 5-51·3 per cent of oil.

INUKUSU OIL [1]

This oil is obtained from the fruit of *Machilus Thunbergii*, S. et Z., a tree belonging to the *Lauraceæ*, and known in Japan by the name Tabu-no-ki. The fruits average 0·8 cm. in diameter and weigh about 0 22 grms. each. The specimens examined contained 4·28 per cent of moisture and 65·09 per cent of oil, and yielded 1·3 per cent of ash. The oil has a brownish colour ; at low temperatures " stearine " is deposited. The oil gave the following characteristics :—

Specific gravity at 25° C.   .   .   .   0·9347
Acid value   .   .   .   19 31
Saponification value   .   241 39
Iodine value (*Wijs*)   .   .   .   66 08 per cent
Refractive index at 25° C.   .   .   1 4646
Reichert-Meissl value   .   .   2 05

PAYENA OIL, KANSIVE OIL

This oil is obtained from the seeds of *Payena oleifera*, a tree known in Burma as " kansive," and belonging to the natural family of *Bassia*. The following characteristics were ascertained by *D. Hooper* [2] and by *Menon* :—

[1] Tsujimoto, *Journ. College of Eng. Tokyo*, 1908, 87.
[2] Private communication to the author.

	Hooper.	Menon.
Fat—		
Specific gravity at 30° C.	0 915	..
Saponification value	198·9	184·5
Iodine value	63·4	58·62
Acid value	26·2	53·9
Fatty Acids—		
Insoluble acid + unsaponifiable (per cent) .	94·5	
Melting point	38° C	

The insoluble fatty acids yielded 35 per cent of ether-insoluble lead salts; the melting point of the fatty acids liberated from these salts. was 55° C.

Kansive oil is used by the inhabitants of Burma for edible and other purposes.

MOWRAH SEED OIL, MOHWRAH BUTTER, MAHUA BUTTER

French—*Huile de Mohwrah, Huile de Mahwrah.* German—*Mowrah-butter, Mahwahbutter, Bassiaol.* Italian—*Burro di Moora.*

For tables of characteristics see pp. 519, 521.

Mowrah seed oil is the fat obtained from the seeds of *Bassia latifolia,* Roxb. = *Illipé latifolia* (Roxb.), Engler = *Bassia villosa,* Wall.,[1] a tree widely distributed in the Northern Provinces of India, and especially in Bengal.

The seeds are smaller still than those of the *B. butyracea*; on an average one seed weighs 0·61 grms. The kernels form 72 per cent of the total seed.

The fat extracted with petroleum ether had saponification value 184·5, iodine value 58·62. After the seed had been extracted with petroleum ether, extraction with common ether yielded a resinous matter having the saponification value 222·6.

The tree is frequently cultivated in East India. This tree gradually disappears towards Calcutta, and is only sparingly met with in the Madras Presidency, its place being taken by *Bassia longifolia* (see p. 522). It should be noted that in India the Mahua or butter tree is also known as "Illipé butter tree," the vernacular names being (amongst many others), *Illipi, Elupa, Kat illipi.* The buds yield a large proportion of invert sugar. The seeds contain 50-55 per cent of fat. In the fresh state the fat is yellow; on exposure to the air the colouring matter is bleached. The oil can also be bleached chemically, as has been done by the author on a large scale by a special process.

Mowrah seed oil has a bitter aromatic taste, and a çharacteristic odour recalling that of cacao beans. The commercial samples contain considerable quantities of free fatty acids, the crystals of which can be recognised under the microscope. The chief constituent of the

[1] Cp. *Les Végétaux utiles de l'Afrique tropicale française,* fascicule ii., par Em. Perrot. Paris, 1907.

solid fatty acids is palmitic acid. A number of samples examined in the author's laboratory contained 17·2-20 per cent of free fatty acids and 2·34 per cent of unsaponifiable matter.

Crossley and Le Sueur have examined a number of genuine specimens, obtained from official sources in India, where this fat is largely used for edible purposes. Their results are reproduced in the following table :—

No.	Origin.	Specific Gravity at 100° C. (Water 100° C = 1)	Melting Point. °C.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Insoluble Acids + Unsaponifiable	Butyro-refracto-meter "Degrees."	Viscosity. Seconds at 140° F.	Compared with water.
1	Bengal	0·8975	24·5	11·70	194·00	62·11	0·44	94·05		97·1	4·24
2	,,	0·8962	26·0	19·15	192·60	64·88			51·8	93·8	4·10
3	Madras	0·8981	25·0	10·33	191·80	67·85				96·9	4·28
4	,,	0·8970	26·5	4·83	190·00	58·53				107·0	4·07
5	,,	0·8964	29·0	8·67	187·40	58·45		94·09		100·6	4·39
6	North-West Provinces	0·8969	23·0	21·20	180·50	63·51				93·9	4·10
7	Central Provinces	0·8971	24·0	17·05	188·80	63·01				96·7	4·22
8	Calcutta	0·8943	25·5	70·82	193·20	58·59	0·88			90·4	3·95
9	Bombay	0·8980	24·0	6·83	190·50	52·43			52·4	96·9	4·25

Mowrah seed oil is an important article of commerce. In India it is employed for various technical purposes, and under the name *Dolia oil* fills the place of tallow where the religious tenets forbid the employment of the latter. Under the name *Me oil* it is applied externally in the treatment of skin diseases.

The table given below shows the exports of Mowrah seeds from British India to the following countries :—

Export of Mowrah Seeds for the Years 1900–1912

Year.	Germany.	France.	Belgium.	United Kingdom.	Other Countries.	Total.
1900	.	80,320	18,147	.	2,422	100,889
1901		5,700	5,261		26	10,987
1902		110,853	25,898	1,426	57,073	195,250
1903		31,386	26,262	2,200	40,707	100,555
1904		71,400	58,648	3,225	31,831	165,104
1905		115,697	48,581	28,931	12,209	205,418
1906	.	49,360	11,667	52,289	5,988	119,304
1907	. .	32,877	6,697	3,375	7,470	50,419
1908	2,200	140,661	88,746	64,922	563	297,092
1909	5,057	61,012	57,490	42,202	400	166,161
1910	155,464	78,821	70,898	2,533	3,705	311,421
1911	126,780	22,085	39,567	15,741	3,184	207,357
1912	274,888	31,518	73,330	3,046	9,568	392,350

The imports of Mowrah seed oil into Germany for the year 1911 from Belgium and China were 167 and 147 tons, and in 1912, 271 and

1050 tons respectively. Mowrah seed oil is used in candle- and soap-making. *Lach* [1] recommends to prepare the fatty acids by the acidification process, as he states they are more readily crystallised than those prepared by saponification with bases. Mowrah oil cannot be used as a substitute for cocoa nut oil in soap-making by the cold process, as it saponifies with difficulty with strong caustic lye. Its soaps are easily salted out. The mowrah seed cakes are poisonous, and can only be used as manure, although attempts have been made to render them edible.[2]

[1] *Die Stearine-Fabrikation*, 1908, 9.
[2] Holstein-Ölwerke G m.b H   French patent 447,894 ; Monhaupt, English patent 23,595/1911 ; United States America patent 1,030,674

Physical and Chemical Characteristics of Mowrah Seed Oil

	Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.	
At ° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms KOH.	Observer.
15, 100 (water 100°, C. = 1)	0·9175, 0·8943-0·8981	Valenta[1], Crossley and Le Sueur	17·25-18·5, 19-22	Valenta, De Negri and Fabris	25·3, 28-31, 23-29	Valenta, De Negri and Fabris, Crossley and Le Sueur	192·8, 190·9, 196·8-192·4, 187·4-191·0, 187·6-190, 196·2	Valenta, De Negri and Fabris, Lewkowitsch, Crossley and Le Sueur, Menon[3], Imp. Inst.
100 (water at 15 = 1)	0·861[2]	Imp. Inst.	...		...			

[1] *Engl. Patgt. Journal*, 251, 461.   [2] Oil from Mauritius.   [3] Determined in the author's laboratory.

Physical and Chemical Characteristics of Mowrah Seed Oil—continued

	Iodine Value		Reichert-Meissl Value		Refractive Index		Viscosity	
	Per cent.	Observer.	cc. ⅒ norm. KOH.	Observer.	At 40° C	Observer.	Seconds at 140° F.	Observer.
	60·4	De Negri and Fabris	1·66, 0·44-0·88	Lewkowitsch, Crossley and Le Sueur	Butyro-refractometer "Degrees," 51·8-52·4	Crossley and Le Sueur	90 4·107	Crossley and Le Sueur
	62·2-63·9, 53·43-67·85	Lewkowitsch, Crossley and Le Sueur	1·6	Menon	...		...	
	63, 52·6	Menon, Imp. Inst.						

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Solidifying Point		Melting Point		Iodine Value	
Per cent	Observer.	°C.	Observer	°C.	Observer	Per cent	Observer
94·76 94·69· 94·95 93·95	Valenta Crossley and Le Sueur Menon	38	Valenta	39·5	Valenta	56·6	Lewko-witsch

The samples examined by *Menon* yielded 13-25 per cent of stearic acid. Arachidic could not be detected.

ILLIPÉ BUTTER

French—*Beurre d'Illipé.*   German—*Illipé Butter.*
Italian—*Burro di Illipé.*

For tables of characteristics see p. 523.

Illipé butter is obtained from the seeds of *Bassia longifolia,* L.,[1] a tree indigenous to the southern part of India. A variety of this Bassia is known as *Illipé malabarica* in the Western Ghats from Kanara to Travancore and the Himalayas, where the tree ascends to an altitude of about 4000 feet. In the south of India this tree is known as the Mowa, or Mahua, or Mahwa tree, the vernacular names being (amongst many others) *Illipi, Elupa, Ellupi, Ilupai.* The commercial Illipé butter is frequently a mixture of true Illipé butter with Mowrah seed oil, the fat from *Bassia latifolia* (cp. p. 518). The seeds resemble those of *Bassia latifolia,* but are a little longer and less rounded. They contain 50-55 per cent of fat. In Ceylon the oil is known as *Me* oil. The cake obtained there by pressing the seeds is exported to the coast under the name " arappo." The poonac of *Bassia longifolia* is used in India as an unguent.

Blumenfeld and Seidel found in a specimen of Illipé butter 1·43 per cent of volatile fatty acids.[2]

Illipé seeds are imported into France and England, where their fat is used in candle-making. According to *Sachs,*[3] Illipé butter is also employed as a chocolate fat. The cake is poisonous, and can only be used as manure.

[1] *Les Végétaux utiles de l'Afrique tropicale française,* fascicule II., par Em. Perrot. Paris, 1907.
[2] *Mitth. d. k. k. technolog. Gewerbe-Museums,* 10, 160.
[3] *Chem. Revue,* 1908, 8.

Physical and Chemical Characteristics of Illipé Butter

Specific Gravity.	Solidifying Point		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.	
	°C.	Observer.	°C	Observer.	Mgrms KOH.	Observer	Per cent.	Observer.		Observer.
0.8930 (water at 100°) Menon	36	Menon	42	Menon	188.2	De Negri and Fabris	50.1	De Negri and Fabris		
0.8586 (water at 15° C.=1) Menon					187.4–188.5[1]	Menon	63.64	Menon	1.35	Menon[2]
							58	,,		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrm KOH.	Observer.		Observer.		Observer.
94.76	Valenta	40 39.7-40.3 (Titer)	De Negri and Fabris Lewkowitsch	45	De Negri and Fabris						
94.00	Menon		Menon			192.1	Menon	291.9	Menon	59.5	Menon

[1] Unsaponifiable matter 2.55 per cent.

[2] Titration number insoluble volatile acids : 0.55.

A sample examined by *Menon* yielded 12-20 per cent of stearic acid. Arachidic acid was absent.

CHAMPACA FAT

French—*Beurre de Champaca.*   German—*Champacafett.*

This fat is obtained in the Dutch Indies from *Melia Champaca.* It is stated by *Sack*[1] to consist of 70 per cent of triolein, and 30 per cent of tripalmitin.

Physical and Chemical Characteristics of Champaca Fat

Specific Gravity.	Melting Point. °C.	Iodine Value.
0.90 5	44-45	60 25 [2]

SHEA BUTTER, BAMBUK BUTTER, KARITÉ OIL, GALAM BUTTER

French—*Beurre de Karité,*[3] *Beurre de Cé,*[3] *Beurre de Shée,*[3] *Huile de Karité.*   German—*Sheabutter, Schibutter, Galambutter.*[4]   Italian—*Burro di Seha.*

For tables of characteristics see p. 528.

This fat is obtained from the seeds of *Bassia Parkii*, De C. (Hássk), (*Butyrospermum Parkii* (G. Don) Kotschy), a tree belonging to the *Sapotaceæ.*[5]

The Karité tree, vernacular names "Kade" (Haussa), "Kedempó" (Kachi), "Krankee," resembling in appearance the American oak, and growing to a height of about 40 feet and having a massive trunk, occurs in enormous quantities on the West Coast of Africa and in the French and English Soudan. It is especially widely distributed in the middle basin of the Niger, and is as characteristic of the regions of the middle Niger as is the palm tree of the lower reaches of the river and of the coast lines. Owing to the wide distribution of the tree, from the West

[1] *De Indische Mercuur*, 1903, April 28.

[2] Calculated by the author from the percentage of olein.

[3] The name "Karité" is the vernacular with the Ouoloff and Toucouleu tribes, whilst the Bambaras and Maluke tribes term it Cé or Sé.

[4] Under the name *Galament* there is also known the nut derived from *Allanblackia floribunda*

[5] Cp. *Les Végétaux utiles de l'Afrique tropicale française*, fascicule ii., par Em. Perrot. Paris, 1907.

Coast of Africa to the Egyptian Soudan, the different specimens of nuts
and fats exported to Europe show some characteristic differences, as the
author has ascertained by examining a large variety of shea nuts. The
tree growing in the Nile basin appears to constitute a special variety,
which is known as *niloticum* (*Kotschy and Chevalier*); the Dahomey tree is
described as var. *Poissoni* (*Chevalier*), whilst the most widely distributed
tree is known as var. *mangifolium* (*Pierre and Chevalier*). The distinction
made in commerce between shea nuts and karité nuts does not appear
to be substantiated by an actual difference in the nuts, as the Lagos
shea nuts exported into the French colonies are re-exported under the
name karité nuts. Although shea butter has been known for a long
time, the first specimens of the nuts having been brought home by
Mungo Park, the first shipment on a commercial scale came to Europe
only in 1877. Some attention is at present being paid to the com-
mercial exploitation of shea butter. According to the Colonial Report
on Southern Nigeria (Lagos) 25 tons of shea butter were exported
in 1904, whereas in 1905, 131 tons were brought by railway from the
up country. In 1906 there were exported 1361 tons of shea nuts
(valued at £12,118) and 363 tons of shea butter (valued at £6000).
The bulk of this is shipped to the French West African colonies. The
exports of shea butter from Togo passed formerly (up to 1901) through
the Gold Coast. Since 1902 the shea butter is shipped to Europe
direct.

The nuts have the size and shape of an ordinary plum. The outer
shell of some specimens is covered with fine fibres, whereas the shell
of nuts coming from the middle Niger district proper presents the
appearance of a polished surface. In some specimens the kernel has
a smooth integument, in others the kernel is covered by a thin layer
of fibre. The proportion of fat in the kernels varies within wide limits
according to the origin of the seeds. In the following table I collate
some recently published numbers obtained by several investigators;
to these are added three determinations made in the author's laboratory
with nuts from authenticated sources.

Description.	Source.	Shells. Per cent.	Kernels. Per cent.	Percentage of Fat in Kernels.	Observer.
..	..	..	..	44	Schindler and Waschata [1]
..	West Africa	...	...	53.5	Drabble [2]
..	?			51.5	,,
Karité nuts	?	.	...	34.0	,,
Shea butter nuts	Southern Nigeria (Oloke Meji Reserve)	29	71	35.96	Lewkowitsch [3]
,,	Northern Nigeria	58.9	41.1 [4]	47.82 [5]	,,
,,	Egyptian Soudan ("Lulu" nuts)	32.5	67.5	44.0	,,
,,	,, ,, ,,	31.0	69.0	57.0	Gordon Memorial College
,,	Tengba (from Lagos)	..	...	51.4	Imperial Institute [6]
,,	Bomo	..	.	48.0	,,
,,	Imported nuts	..		41.4	,,
,,	Kiln-dried nuts			26.2	,,
,,	"Giddamchi" [7]		.	48.6	,,
,,	"Eka" [7]	.	.	52.4	,,

Exports of Shea Nuts and Shea Butter from Nigeria

Year.	Shea Nuts.	Shea Butter.
	Tons.	Tons.
1908	3967	320
1909	9728	309
1910	4464	340
1911	3629	248
1912	7756	180
1913	9420	120

Older statements with regard to the yield of fat from the seeds refer to individual specimens only, and have therefore no general signification. Nor can the statement in older text-books that shea butter is characterised by a grey or greyish-white colour be maintained.

The fat is extracted by the natives by pounding the kernels and boiling the paste with water. The fat rises to the surface and is skimmed off into large calabashes, in which it is carried to the river, where traders collect it and take it down to the coast.

[1] *Zeitschr. f. angew. Chem.*, 1905, 305.

[2] *Quart. Journ. Inst. Comm. Research in the Tropics* (Liverpool University), 1906, i. 67. [3] Unpublished determinations.

[4] In this case the nuts were still covered with the fibrous layer. The percentage of kernels calculated to the smooth nuts, freed from the fibrous layer, would be 51.4. The 58.9 per cent in the above table represent therefore shells and fibrous layers added together. The latter formed about 20 per cent of the total fruits.

[5] The kernels of another specimen of Lulu nuts yielded (in the Imperial Institute) 47.2 per cent of fat. [6] *Bull. Imp. Inst.*, 1909, 370.

[7] Northern Nigeria. The nuts range from 1.5 to 2.5 inches in length, whereas the "Giddamchi" nuts are on the average 1.4 inches long.

Little care being taken in the preparation, much of the shea butter that comes to Europe has a grey or whitish-grey colour and is characterised by a strong indiarubber-like odour and taste. More care is taken by the natives in the preparation of shea butter for their own purposes, only the freshest kernels being used. The fat so obtained is made up into cakes and wrapped round with leaves to prevent it from becoming rancid. Preserved in this manner, the fat will keep fresh for several months. In proof of the statement that the grey colour must not be considered characteristic of shea butter, it may be mentioned that a number of shea butters extracted in the author's laboratory from different nuts furnished a pale yellow fat with not quite so pronounced an indiarubber-like taste as commercial samples possess. The fat expressed in this country from shea nuts is known as "shea nut oil." The press cake contains only 1·5 per cent of nitrogen; its high proportion of carbohydrates renders it useful for making "compound" cakes.

Pfaff's [1] statement that shea butter consists of tristearin and triolein, in the proportion of seven parts of the former to three parts of the latter, is not borne out by the iodine values ascertained in the author's laboratory.

The author has therefore examined a number of different shea butters with a view to determine directly the percentage of stearic acid. This was found to vary from 33·7 per cent to 37·3 per cent.

Hébert [2] examined a sample of karité seeds and obtained the following figures :—

Specific gravity at 32° C. . .	0·900
Solidifying point, ° C. . . .	19
Melting point, ° C. .	32
Saponification value	196
Iodine value	69·6
Reichert-Meissl value	1·1
Insoluble acids + unsaponifiable (per cent)	95·25

The sample had the acid value 7·7. The insoluble acids were separated by the lead-salt-ether method into 33 per cent liquid acids and 67 per cent solid, the latter having the melting point 67-68° C.

From the fractional precipitation of the fatty acids, the solid acids appear to consist of arachidic, stearic, and palmitic acids.

Southcombe [3] examined a native-prepared shea butter, having the iodine value 57·6, by separating the solid acids from the liquid acids and fractionally precipitating the former. He states the composition of the mixed fatty acids to be as follows :—Oleic acid 60 per cent, stearic acid 30-35 per cent, lauric acid 3-4 per cent; palmitic acid was not identified. The iodine value of the liquid acids was found to be 90·8.

Shea butter plays a very important part in the economy of the native as an edible fat, as a burning oil (in the crude native lamp), and for cosmetic purposes.

[1] *Muspratt's Chemie*, 4th edition, vol. iii. p. 574.
[2] *Les Matières grasses*, 1911, 2170.
[3] *Journ. Soc. Chem. Ind.*, 1909, 499.

Physical and Chemical Characteristics of Shea Butter

Specific Gravity		Solidifying Point.		Melting Point.		Saponification Value		Iodine Value		Reichert-Meissl Value.	
°C	Observer.	°C.	Observer.	°C	Observer	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. 1/10 KOH.	Observer.
15 0·9175	Valenta	17-18	Valenta	25·3	Valenta	192·3	Valenta	56·2-56·9	Lewkowitsch	1·4-2·6	Imperial Institute
„ 0·9177	Milliau			23-23·3	Stohmann	171·8-187·2	Lewkowitsch Kassler	67·2	Milliau		
0·8594	Imperial					182·4				1·15	Southcombe
0·869	Institute					179·0-184	Imperial Institute	54·62·9	Imperial Institute		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Solidifying Point		Melting Point		Iodine Value.		Liquid Fatty Acids	
Per cent	Observer.	°C	Observer.	°C.	Observer.	Per cent	Observer.		
94·7	Valenta	38	Valenta	39·5	Valenta	56·57·2	Lewkowitsch		
96·5	Imperial Institute	52·5	Milliau	56	Stohmann	55·6	Kassler		
				56·5	Milliau				
	Titer Test.							99·6	Southcombe
	53·8	Lewkowitsch							
	48·6	Kassler							

¹ The unsaponifiable matter in this sample amounted to 9·7 per cent.

According to the state of freshness of the fat the proportion of free fatty acids varies. The samples examined in the author's laboratory had acid values varying from 12·5 to 29. The saponification value also varies considerably in different specimens, as is shown by the numbers recorded in the table of characteristics under the heading "saponification value." This is due to the variation in the amount of unsaponifiable matter, which in the different specimens examined by the author was found to be from 3·6 to 9·7 per cent. The unsaponifiable matter seems to cause the indiarubber-like smell and taste. A process for the isolation of this substance (shea gutta?) has been patented by *Rocca, Tassy and Roux*.[1]

The considerable amount of unsaponifiable matter in shea butter militates against its being used for soap-making purposes. Its india-rubber-like taste would seem to preclude the hope of preparing an edible fat from shea butter.[2]

Shea butter would seem to form a good raw material for candle-making, provided the fatty acids crystallise readily. *Kassler*[3] obtained, by hydrolysing shea butter in an autoclave under a pressure of 9 atmospheres with 3 per cent of magnesia, 92 per cent of fatty acids of the solidifying point 48·4° C. On distilling the fatty acids on a large scale, the samples taken from the condenser during the first twenty-four hours had solidifying points from 48·9° to 51·3° C., and iodine values from 17·03 to 51·32. In the following six hours of the distillation process small amounts of hydrocarbons were formed, increasing from 0·34 per cent to 5·07 per cent.

NJAVE OIL, NJAVE BUTTER, NARI OIL, NOUMGOU OIL, ADJAB OIL

French—*Beurre de Njave (Djave)*; *huile de Noumgou*.
German—*Njave Butter*; *Njariol*; *Adjabfett*; *Jabifett*.
Italian—*Olio di Njave*.

This oil is obtained from the seeds of *Mimusops Njave* or *Djave* (De Lanessan), Engler [Synonyms are :— *Bassia Djave*, De Lanessan ; *Bassia toxisperma*, Raoul ; *Tieghemella africana*, Pierre ; *Baillonella toxisperma*, Pierre ; *Baillonella Djave*, Pierre ; *Tieghemella Jollyana*, Pierre], a tree[4] belonging to the family of the *Sapotaceæ*, which also includes *Bassia Parkii*, yielding the shea butter. The tree is indigenous to West Africa, Cameroons, Gaboon, Nigeria, and furnishes, like most trees belonging to the *Sapotaceæ*, gutta-percha (cp. "Surin Fat," below[5]). In the Cameroons the tree is known to the natives as "Noum-

[1] French patent 361,368 ; German patent 191,736. Cp. also D. Spence, *Quart Journ. Inst. Comm. Research in the Tropics* (Liverpool University), 1908, 61.
[2] At the Marseilles Colonial Exhibition of 1906 there was exhibited an edible fat stated to have been prepared from shea butter and having the melting point 38-39° C. The author was, however, not afforded an opportunity of tasting it.
[3] *Seifensieder Zeit.*, 1902, 311.
[4] *Les Végétaux utiles de l'Afrique tropicale française*, fascicule ii., E. Perrot. Paris, 1907.
[5] The wood is known in commerce as Cameroon mahogany.

gou," and as Adjab or Njabi, and in Gaboon as "Njave" or "Djave." The fruits are termed by the natives "Ouréré." In the Gold Coast Colony the fruits are known as " Bako (Abeku) Nuts " [1] ("Mahogany Nuts ").

The natives (the *Jaundes* and the *Ngumbas*) prepare the oil by drying the seeds over fire and breaking the shell with stones. The kernels are then pounded in a mortar or comminuted by rubbing between stones. The mass is then boiled out with water, the fat is skimmed off by hand and freed from the bulk of water by squeezing between the hands and then subjecting it to a somewhat stronger pressure in baskets, by heaping stones on the mass. By this process an extremely poisonous saponin,[2] contained in the fresh seeds, is completely removed, so that the fat can be used for culinary purposes. The presscakes (in case the seeds should be expressed on a large scale) would retain the poisonous substance to a large extent and hence be valueless as a feeding cake. *Fickendey* states that the saponin can be removed completely by boiling out with water. Thereby a considerable amount of nutritive substances would also be removed.

The weight of the individual nuts varies between 10 and 21·6 grms, one-third of which is made up by the shell. The kernels, forming from 65 to 72 per cent of the nuts, contain 43-64 per cent of a white fat, which is solid at the ordinary temperature.[3] The highest numbers due to *Fickendey* [2] refer to fresh nuts. " Stearine " commences to separate at 31° C.; at 19° the whole mass is solid. The specimen of Njave butter examined by *Wedemeyer* [3] had undergone a considerable amount of hydrolysis, for it had the acid value 38·1 ; the amount of insoluble fatty acids + unsaponifiable was therefore somewhat high, viz 96·1, of which the unsaponifiable matter formed 3·66 per cent. The specimen examined by *Freundlich* [4] had the acid value 13·8 ; and the amount of unsaponifiable matter was 2·20. The specimen examined in the *Imperial Institute* had the acid value 25·3, and contained 2·6 per cent of unsaponifiable matter, the specimen examined by *Fickendey* had the acid value 18·2, and contained 2·56 per cent of unsaponifiable matter.

The following characteristics were determined by the observers named :—

[1] Catalogue of Exhibits of the Gold Coast Colony, Franco-British Exhibition, 1908.
[2] Fickendey, *Der Tropenpflanzer*, 1910, 29.
[3] *Chem. Revue*, 1907, 35.
[4] *Ibid.*, 1908, 79 ; 106.

Physical and Chemical Characteristics of Njave Oil

Specific Gravity.		Saponification Value	Iodine Value	Reichert-Meissl Value	Acetyl Value (Lewkowitsch)	Saponification Value of Acetylated Fat.	Maumené Test °C.	Butyro-refractometer at 40° C.	Observer.
°C.									
40 15 (water at 15=1)	0·8979 0·9167	185·3 182·5	56·1 56	1·2 0·7	13·4 15·7¹, 7·1²	195·3	55	52 "degrees"	Wedemeyer Freundlich
100 15 (water at 15·5=1)	0·860	187·6	56·2	Nil	··	··	··	··	Imp. Inst.³
50 15	0·9172 0·9137	188·6 186·7	57·2 56·2	0·8 0·8	12·9	··	··	··	Fickendey Wagner and Oestermann⁴

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Unsaponifiable.	Solidifying Point °C.	Melting Point °C.	Neutralisation Value.	Mean Molecular Weight	Observer.
96·1	44·1⁵	46·6	201·7	278·3	Wedemeyer
··	46·⁶	··	··	284·6	Freundlich
	47·8⁵				Imp. Inst.³
94·76	47	51	198·5	282·7	Fickendey
	46·3	53·0	195·6	287·1	Wagner and Oestermann⁴

[1] Distillation process — [2] Filtration process.
[3] Bull. Imp. Inst., 1908, 374.
[4] Zeits. f. Unters. d. Nahrgs- u. Genussm., 1912, 332.
[5] The insoluble fatty acids included the unsaponifiable matter. At any rate no statement to the contrary has been made by the author.
[6] The insoluble fatty acids were free from unsaponifiable matter.

The statement made by *Fickendey* that Njave nuts are poisonous is controverted by *Wagner and Oestermann*.[1] This point requires further elucidation. These observers found. 2·56 per cent of unsaponifiable matter but could not detect phytosterol.

The oil from *Dumoria Heckeli*[2] is described by *Pierre* as *Tieghemella Heckeliana*, and renamed by *Chevalier* "*Dumoria Heckeli*." An examination on a large scale gave the following result :—

Yield of fatty acids by saponification, per cent	95
Solidifying point of same, ° C.	52·4
Yield of "saponification stearine," per cent	55·30
Solidifying point of same, ° C.	66
Yield of fatty acids by distillation, per cent	91
Solidifying point of same, ° C.	56·8
Yield of "distillation stearine," per cent	69·55
Solidifying point of same, ° C.	62·5

The cake, according to *Heckel*, is extremely bitter and contains a very low proportion of nitrogen.

A specimen examined by *Hébert*[3] had the following characteristics :—

Yield of fat from the kernels, per cent .	40
Yield of fat from the seeds ,, ..	14
Oil—	
Specific gravity at 15° C.	0 956
Melting point, ° C. .	34
Saponification value	188
Iodine value	56·4
Acid value .	5 6
Fatty Acids—	
Insoluble acids + unsaponifiable, per cent.	96 8
Melting point, ° C. .	60

AOUARA OIL—TUCUM OIL [4]

French—*Huile d'aouara, Huile de Tucum.* German—*Aouaraol, Tucumol.* Italian—*Olio di aouara, Olio di tucum.*

This oil is obtained from the aouara palm, *Astrocaryum vulgare*, Martens, which occurs in French Guiana. In older text-books this oil is frequently described as a variety of palm oil. (The French colonists distinguish two kinds of oil palms : *Aouara d'Afrique*, or *A. de Guinée* (*Elæis guineensis*) and *Aouara de la Guayane* (*Astrocaryum vulgare*), and therefore the corresponding oils are known as Aouara oil of Guinea and Aouara oil of Guayana.[5]

As in the case of the true African oil-palm, the fruits of the aouara palm grow in bunches. The fruits are oviform, and consist of a fleshy, fibrous pulp, in which is embedded the aouara oil, and of a very hard,

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1912, 332.
[2] Heckel, *Les Matières grasses*, 1912, 2791.
[3] *Les Matières grasses*, 1912, 2814.
[4] Although this fat has a higher iodine value than the preceding fats, its close relationship to palm oil justifies its position here.
[5] Duchesne, *Catalogue des colonies françaises*, 1867, p. 88.

black nut (harder than the true palm nut), which contains a hard, irregular kernel.

The oil obtained from the kernel differs from that recovered from the fleshy part in the same manner as palm kernel oil differs from palm oil. The kernel oil will therefore be described separately (see below, under " Cocoa Nut Oil Group ").

The fruits examined by *Bontoux*[1] were dry, although well preserved. Fifty fruits weighed 860 grms., and consisted of fibrous pulp, 24·2 per cent ; shells, 50·4 per cent ; kernels, 25·4 per cent. The fibrous pulp gave on extraction with petroleum ether 34 per cent of a golden-yellow,[2] fluid fat, from which " stearine " separated on cooling. The acid value of this fat was 31·4. The following characteristics were ascertained by *Bontoux* :

Specific gravity at 15° C.	0·916
Saponification value	196·5-197·2
Iodine value	74·8-75·7
Fatty acids + unsaponifiable, per cent	95·0
Titer test of the fatty acids, ° C.	32·2
Neutralisation value of the fatty acids	198·5-199·7
Mean molecular weight	281·0

The oil is prepared by the natives in the same manner as palm oil is obtained in West Africa. It serves for culinary purposes.

PALM OIL

French—*Huile de palme.* German—*Palmöl.*[3]
Italian—*Olio di palma.*

For tables of characteristics see pp. 540, 541.

Palm oil is obtained from the fruit of the palm tree *Elæis guineensis*, L. (Jacq.), which form vast forests along the West Coast of Africa, extending between Gambia and St. Paul de Loanda. The West Coast of Africa is practically the only source of palm oil. *Elæis guineensis* forms a very large number of subspecies for a description of which the reader is referred to *A. Chevalier* and to *J. Adam*.

Another species of the palm tree, viz. *Elæis melanococca*, Gart. (*Alfonsia oleifera*, Humb.), is cultivated in South America (Venezuela), in the province Amensis in Brazil, in the West Indies, in Java, and North Burmah. But the quantities of oil obtained from this tree are

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[1] Cp. Lewkowitsch, *Technologie et analyse chimiques des huiles, graisses et cires,* traduit par E Bontoux, Paris, vol ii. p. 1043.

[2] In the older literature the oil is stated to have a vermilion red colour, which persists, even on keeping the fat for years. It is also stated (Wiesner, *Die Rohstoffe des Pflanzenreichs,* 1900, vol. i. 488) that the colouring matter cannot be removed by boiling with water, but is " bleached " by heating the fat whilst it is exposed to the air; the colouring matter is also said to be destroyed by oxidising agents

[3] In the German literature the name " palm oil " is given promiscuously to all fats derived from plants belonging to the palm family, so that not only palm nut oil but also cocoa nut oil is frequently referred to as palm oil. Such misnomers are apt to lead to confusion.

very small ; at any rate they do not reach the European market and it appears very doubtful whether the oil is really palm oil or rather a fat obtained from a palm. The American palm is smaller than the African ; its fruits are reddish. To this colour is due the local name " Coroza [1] Colorado."

Keil states that the oil palm occurs in a small district situated in the North and North East of Lake Tanganyika. Attempts are being made to cultivate the tree in the Malay Peninsula.

The favourite habitat of the palm tree is the open country or bush-land, and it grows frequently where the natives have cleared the virgin forest. The tree is characteristic of the coast line and the lower reaches of the rivers. It will grow in all soils, but does not bear well at a higher altitude than 3000 feet. Under favourable conditions, *e.g.* when the plant grows in rich alluvial land, the tree forms a trunk when five [2] years old, and then begins to yield fruit ; when grown in hilly country the plant does not commence to bear fruit before the sixth or seventh year. In the first year or two of bearing fruit only a few bunches are obtained. The yield then increases and the palm tree yields its full harvest in its twelfth year. This rate of yield is then continued throughout the life of the palm tree, which lasts for a further fifty to sixty years. There are two main crops ; in some regions four, or even five, are gathered in the year. The chief crop and the one yielding the better oil is that gathered in the early months of the year. Hence the best oil arrives in Europe after June. The heaviest ship-ments of palm oil come from the coast between May and August ; those from the Gold Coast, Dahomey, and the Lagos districts are earlier than those from Bonny, Opobo, Old Calabar, etc. (termed " river oils "). The second crop is gathered in October and November and is less abundant than the first crop. The chief supply from the Niger district (Southern Nigeria) arrives in Europe from October to February.

Many writers have confused the term palm nut with the " fruit," *i.e* the whole fruit consisting of an epidermis, fleshy part of the fruit and the seed, the latter forming a hard nut, consisting of shell and kernel (seed kernel).

Palm oil is obtained from the outside fleshy portion of the ripe fruit. Owing to climatic conditions, the process of extraction, which has been hitherto practised exclusively by the natives, is an exceed-ingly crude one. When the fruits (" abe ") ripen the men climb up the trees and cut off the bunches with " matchets." [3] Owing to the height from which the bunches fall, a large quantity of the fruit is bruised, which naturally leads to rapid fermentation and to hydrolysis of the oil. The bunches are stored for three or four days, when the women and children pick the fruit from the bunches [4] and throw it

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[1] In Guatemala the cohune nut is also termed "Coroza."

[2] If the tree is kept free of weeds and creepers and of beetle-grubs, and properly trimmed twice a year, it begins to bear after the fourth year.

[3] This name is a corruption of the Spanish word "macheta," *i.e.* cutlass.

[4] A machine for detaching the fruit from the bunches is patented under German patent 248,544 ; cp. also Haake, English patent 26,032, 1912.

into a hole dug in the ground and lined with leaves. The flesh of the
fruit is at this time hard, and before the kernels can be separated the
flesh must be softened. This is done by sprinkling water on the fruit,
covering it over with more (plantain or banana) leaves weighted by
stones and wood, and leaving it from two weeks to three months.
During this period fermentation sets in, which causes the fleshy part
of the fruit to become soft, so that the kernel—palm nut—can be
removed more readily. This is done by men, who place the fermented
fruits in a mortar, roughly made by lining a hole made in the ground
with large, flat stones. The fruit is then beaten with long wooden
pestles and the pulpy mass is put into a rough net, to which several
sticks are fastened. By turning the sticks in opposite directions the
oil is squeezed out, or the beaten pulp together with the nuts[1] is
taken out by women and children and placed over another hole, the
sides of which have been cemented by plastering with a mixture of
palm oil and wood ashes. This pulpy mass is then allowed to rest
for a week. During this time the oil drains into the cemented hole,
from which it is ladled out into large calabashes of a size to make up
one load.

The oil so prepared represents a superior kind of product. Women
and children then pick out the nuts from the pulp, mix the pulp with
water and place it in large iron cauldrons, where the whole mass is
well boiled and stirred till the oil rises to the top. The oil is skimmed
off and in some regions mixed with the first extracted oil or put into
separate vessels for the market. Finally, the residue is placed in a
bag and squeezed over a hole so as to force out the liquid, from which
more oil rises to the top. This oil contains a large quantity of water,
and is again boiled out, skimmed off, and placed in calabashes.

The oil is carried—mostly by women—to the nearest coast or river
station, where traders collect it in large barrels, and take it down to
the coast station. There the oil frequently undergoes a rough puri-
fication by being boiled up with water, and strained through sieves
into barrels ready for shipment.

A special kind of oil is prepared by boiling the freshly picked fruit
with water and preserving the skimmed-off oil for food purposes. This
oil is prepared for each household, and is not exported. It is known
as " Chop Oil."

In Gambia the fruit when ripe is cut down and the husk-like cover-
ing of each fruit is removed. The clean fruit is placed in a pot and
boiled with water until the fibrous pericarp is sufficiently loosened.
No fermentation is therefore allowed to assist the operation. When
the pericarp has swollen and is therefore more easily detached from
the stone, the whole is placed in a mortar and pounded, until the kernel
stones can be removed.

It will readily be understood that this crude process, which is
practised with more or less important modifications in the same manner

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[1] The whole fruit is frequently termed by writers on this subject palm nut. In this
work the whole fruit, i.e. the palm nut surrounded by the fleshy part and forming the
" palm fruit," is clearly differentiated from the palm nut (seeds) which consists of a hard
shell, enclosing the oleaginous palm kernel.

in all the African villages,[1] and seems to be a survival of the process by which olive oil has been produced in North Africa up to a few decades ago, is an extremely wasteful one; enormous quantities of oil are lost in consequence of this mode of extraction. It has been attempted to introduce portable machinery for the more economical working up of palm oil, and there are in the market several machines of this kind.[2] One of these constructed by *Haake* [3] consists of a pulping machine and a hydraulic press. In the pulping machine the fruit is treated in the hot and the fleshy part is stripped off the nuts. The pulp is then expressed in the hydraulic press. Owing to the fact that the recovery of palm oil is a kind of house industry, and to the distance of the villages from the river, there is very little prospect of machinery being introduced to a notable extent in the near future. Private information given to the author states that the working of *Haake's* machines has not been attended with success. A similar machine was patented recently by S. C. Phillips.[4] A process recently introduced into Togo, by which the fruits are heated for some time at $100°$ C. within two hours of gathering and then mechanically pounded and expressed once, is stated to yield a much better oil as regards the content of free fatty acids than the older methods.[5]

In the above described processes of preparing palm oil the seeds remain intact.[6]

To produce one ton of oil, 1400 bunches of fruit are required in the best managed districts. (A bunch in the state of full ripeness bears from 1000 to 2000 fruits weighing from 22 to 44 pounds.) Besides the oil, about two tons of kernels are obtained. In the more remote villages where the work is carried on less carefully, up to 6000 bunches are stated to be required for one ton of oil.

The average weight of the fruit, as ascertained at the Botanic Gardens at Victoria (Cameroons) is 6·6 grms., of which the pulp forms 2·47 grms. The average weight of the kernels is 0·96 grms., whilst the shells of the seeds weigh on the average 3·17 grms. According to these figures, 100 grms. of fruit would yield *fruit pulp* 37·5 per cent, *seeds* 62·5 per cent. The 37·5 per cent of pulp is made up of 32·8 per cent of palm oil, the remaining 4·7 per cent being water and waste fibre. The 62·5 per cent of seeds consists of 47·92 per cent of shells and 14·58 per cent of kernels, which contain about 50 per cent of fat (see p. 537). Careful experiments made with fruit of the average weight of 6·6 grms. showed that whereas the natives require 1370 bunches for the production of one ton of oil, the same quantity of oil could be obtained from 405 bunches consisting of 1650 fruits each

[1] For a description of the processes in vogue in Dahomey, cp. Lewkowitsch, *Technologie et analyse chimiques des huiles, graisses et cires,* traduit par E. Bontoux, Paris, vol. ii. p. 1046. Cp. also Soskin, *Chem. Revue,* 1909, 290.

[2] Hawkins, English patent 20,061, 1911.

[3] *Chem. Revue,* 1910, 53.

[4] English patent 9733, 1906. Cp. also J. H. Eglen, English patent 3357, 1909.

[5] Kenner, *Verhandl. Ölrohstoffkommission der Kolon.-Wirtsch. Komitees,* 1913, 17.

[6] A proposal to crush fruit and kernels together so as to obtain a mixed oil (pulp oil and kernel oil) has recently been patented by A. Hallet and Spinnael, French patent 321,918.

(exclusive of the kernels). The yield of oil depends to some extent
on the care which the cultivator gives the tree, on the nature of the
soil, and the season.

From these experiments it follows that the natives lose about two-
thirds of the oil obtainable. Of course these last figures can only
be taken as typical for the country from which the palm fruits have
been taken, as the size of the fruit and yield varies considerably. Thus
the pulp forms according to the variety of the palm tree, 27-70 per
cent of the total fruit, whilst the kernels, freed from the shells, form
9-25 per cent. *Fendler* [1] examined four varieties of palm fruits from
the Cameroons locally known under the names *De, De-de bakui, Se-de,*
and *Afa-de.* The following are the results of his examination :—

The fleshy part of fruit contains —	1. De.	2 De-de bakui.	3 Se-de.	4 Afa-de.
	Per cent.	Per cent.	Per cent.	Per cent.
Oil	66 5	58·5	59·2	62 9
Moisture	5 3	5·7	6 9	5 6

Besides these four recognised varieties of palm trees, there exist
in the Cameroons two other varieties, termed the small-fruited and
large-fruited " Lisombe palm," [2] which differ from the ordinary palm
tree in that the shells enclosing the kernel are more brittle than those
of the ordinary palm nuts. The following table gives some informa-
tion as to the Lisombe varieties,[3] contrasted with the ordinary palm
fruit from Victoria in the Cameroons, and palm fruits from other regions
of West Africa :—

Origin.	Variety.	Pulp in whole fruit.	Palm Oil in whole fruit.	Palm Oil contained in pulp.	Kernel in whole fruit.	Palm-kernel Oil in whole fruit.	Oil contained in kernel.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Cameroons	Small-fruited Lisombe .	71 0	32 66	46 0	9 54	4·91	49 2
,,	Large-fruited Lisombe, ripe .	71 0	44 41	62 5	12·5	6·15	48·0
,,	Large-fruited Lisombe, unripe	61 5	40·35	60 5	17·27	8 5	49 2
,,	Ordinary Palm .	37 5	22 64	60 3	14·58	7·13	48 9
Dahomey	De palm, fresh .		21 2	50	..	9·3	49
,,	Kissede palm, fresh . .		26·5	54		9 3	49
Ivory Coast			16-18	45-52		9·4-11	46-48
Guiana	.		18-24	53-57	..	9·12	43-47

The following table due to *Lommel* [4] gives some particulars of the
fruits and kernels obtained from the East African palms :—

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[1] *Berichte d. Deut. Pharm. Gesell.,* 1903, 115.

[2] Preuss, *Der Tropenpflanzer.* Cp. also Smend, *Der Tropenpflanzer,* xii. No. 6.

[3] According to Drabble (*Quart. Journ. Inst. Comm. Research in the Tropics,* 1908,
18), the Lisombe (Issombe) palm resembles the Abobo-be palm of the Gold Coast.

[4] *Der Pflanzer,* 1910, 290.

Origin.	Pulp.	Kernels.	Shells.	Average Weight of a Fruit.	Ratio of Kernel to Shell.	Palm Oil in the Fruit.	Kernel Oil in Fruit.	Palm Oil in Pulp.	Kernel Oil in Kernel.	Average amount of Palm Oil in Fruit.
	Per cent.	Per cent.	Per cent.			Per cent.	Per cent.	Per cent	Per cent	Per cent.
Mohoro tree (I.)	18.3	33.0	48.7	4.16	1 : 1.48	6.26	11.51	34.11	34.90	} 6.82
Mohoro tree (II.)	12.2	32.8	56.0	3.46	1 : 1.67	7.39	14.93	60.54	45.45	
Magrotto, large fruits	23.8	19.5	55.5	10.9	1 : 2.91	13.82	7.45	58.06	38.26	} 17.89
Magrotto, small fruits	73.6	..	26.4	1.8	.	40.0	6.8	54.43	..	
Kiomoni	34.8	22.9	46.0	9.7	1 1.84	23.6		67.67	29.67	..

In the Togo district (Misahöhe, German colony) there occurs besides the ordinary species called locally *E-le* and *De-ti*, also another species, called locally *Séddé*, which is poorer in oil, and is perhaps identical with the *Se-de* species described by *Fendler*. The fruits from the first kind are differentiated from the latter by their ovoid shape and bright colour. Besides this species there also occurs another variety rich in oil—termed by the natives *Klu-dé*. This species, however, does not provide palm oil for export.

At the Gold Coast there occur four well-marked forms of oil-palms which are described by *Evans*[1] as follows:—

(1) *Abetumtum* or *Yue Yumu*, bearing black fruits which yield 13·77 per cent of oil.

(2) *Abepa* or *Yue*, the fruits of which yield 11·2 per cent of oil.

(3) *Abedam* or *Yue-hlem*, bearing reddish-yellow fruits which are larger than those of the other varieties. The fruits yield 11·2 per cent of oil.

(4) *Abobo-be* or *Yue Wyiam*, which represents the best variety on the Gold Coast. The shell of the kernel is much thinner than that of all the other varieties, and is so soft that it can be cracked with the teeth. (In this respect it resembles the Lasombe palm in the Cameroons.) The fruits are reddish-black, and yield 19·3 per cent of oil.

The size of the fruits of the palms growing wild in German East Africa is very much smaller than that of the fruits from the West African varieties.[2] The oil contained in the East African fruits amounted to 4·8 per cent only.

Further investigations made by *J. Anderson*, Director of Botanical Gardens, Aburi, Gold Coast, in conjunction with *Evans*, confirm these variations with the following additions:—

Aoe-fitaa ("white palm nut"): Fruits, large, colour white streaked with black. The oil obtained from this variety is yellow in colour, and quite distinct from other commercial palm oils; yield 15 per cent of oil. Iodine value 44-45 per cent.[3]

Abuba-be: This variety resembles *Abobo-be* in appearance, and the shell of the kernel is also soft, but the pericarp is much more fleshy, and the yield is greater, viz. 25 per cent of oil.

Adi-be: Fruits, large, colour brick-red. This variety has a very fleshy pericarp, and the yield obtained is 28 per cent of oil.

Abe-ohene ("king of palms")[4]: This variety has a medium-sized fruit, bright-red in colour, streaked with black; yield 15 per cent of oil.

It would appear from the above that *Abobo-be, Abubu-be,* and *Adi-be*—all three varieties are also known as *Be-nim* or *Abe-nim* and *Abuborn* (they contain no kernel)—are the best varieties to cultivate, but at the present time the natives of the Gold Coast do not appear to plant any particular variety.

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[1] *Quart. Journ. Inst. Comm. Research in the Tropics,* 1908, 18.
[2] Lommel, *Der Tropenpflanzer,* 1910, 39.
[3] *Bull. Imp. Inst.,* 1909 (7), 357.
[4] In Southern Nigeria the "King palm" is known as *Af-frako-jub.*

Physical and Chemical Characteristics of Palm Oil

Specific Gravity		Solidifying Point		Melting Point		Saponification Value		Iodine Value	
°C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms KOH.	Observer.	Per cent.	Observer.
15	0·9209-0·9245 Tate	33·1	Fendler	From 27 to 42·5 according to age and origin of the oil		202-202·5	Valenta	53	Tolman and Munson
18	0·946 Stuhrell	39·2	,,	42·1	Fendler	196·3	Moore	56	Lewkowitsch
50	0·8930 Allen	37·3	,,	43·2	,,	201-202	Thorner	53·38·1	Fendler
(water 15·5=1) 98·99	0·8586 ,,	31·4	,,	41·3	,,	205·521	Fendler	53·15·2	,,
(water 15·5=1)				35·4		203·782	,,	55·44·3	,,
						201·93	,,	55·68·4	,,
						200·84	,,		

Physical and Chemical Characteristics of Palm Oil—continued

Reichert-Meissl Value.		Refractive Index.	
c.c. norm. KOH.	Observer.	At 60° C.	Observer.
1·07	Clapham⁵	1·4510	Thorner
0·86·1	Fendler		
0·74·2	,,		
1·87·3	,,		
0·90·4	,,		

1 From De palm; the oil contained 54·06 per cent free fatty acids (calculated to oleic).
2 From De-de baku palm; ,, ,, 55·07 ,, ,, ,, ,,
3 From Se-de palm; ,, ,, 55·38 ,, ,, ,, ,,
4 From Afa-de palm. ,, ,, 57·18 ,, ,, ,, ,,
5 Determined in the author's laboratory with bleached palm oil.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
Per cent.	Observer	°C.		Observer	°C.	Observer	°C.	Observer	Mgrms KOH.	Observer		Observer	Per cent.	Observer
			Observer											
95.6	Hehner	98-99 (water 15.5=1)	0.8369	Allen	Average 44.13	De Schepper and Geitel	47.75	Valenta	206.5-207.3	Valenta	273	Tate	53.3	Thorner
94 2.97	Tate	1.0 (water 100=1)	0.8701	Arch-butt	As a rule 44.5-45, rarely 39-41 or 45.5-46.2	Valenta	47.8	Hübl	204	Thorner	270	Allen		
					42.5-43	Hübl	50	Allen					Liquid Fatty Acids.	
					42.7	Allen							94.6	Lewkowitsch
					45.5	Lewkowitsch							29	Tolman and Munson
					Highest 45.4-45.5 Lowest 35.8-35.9	"								

Besides these varieties, there is also the *Abe-Kotoko*[1] ("porcupine oil palm"), so called from the long spikes in the bunch protecting the drupe ("*abe*"), and *Mina-be* ("broom oil palm"), which supplies materials for the best brooms.[2]

In a report made by a Commission appointed in 1887, the statement occurs that three varieties are distinguished by having orange, red, and black fruits respectively; the first gives the finest oil, but contains small kernels, the other varieties give less oil but have larger nuts.

The fruits obtained from Benin and Calabar were found by *Drabble* to contain 24·8 and 29 per cent respectively of palm oil.

The following table[3] furnishes an instructive comparison of palm fruits from various districts :—

Ratio of	New Calabar	Old Calabar	Lagos	Dixcove	Warri	Benin
	Per cent.	Per cent	Per cent.	Per cent	Per cent	Per cent
Pericarp[4] to whole fruit	...	38·76	24·65	30·89	23·36	35·67
Pericarp fat „ „	...	29·02	14·38	20·94	14·01	24·86
Pericarp fat to whole pericarp .		74·88	58·33	67·8	60·0	69·69
Kernel to kernel and shell .	20·4	22·81	25·0	31·06	24·17	20·17
Kernel oil to kernel and shell . .	5·2	4·7	5·0	12·42	4·81	5·01
Kernel oil to kernel	25·0	20·58	20·0	35·0	21·05	25·0
Average volume of fruit in c.c.		7·2	4·0	5·2	6·7	7·5

The following samples of palm fruits and oil were obtained from Dahomey and examined by *Hébert*.[5] The oil was obtained by extraction from the fruits with petroleum ether. All the oils are used by the natives as food with the exception of that obtained from the variety *Repanda* which is said to cause headache and sickness :—

[1] *Abe* or *be* means oil palm fruit, *bobo* = crack with the teeth, *babu* = break in pieces, *Adi-be* = palm nut for eating.

[2] For a more complete list of vernacular names cp. A. Chevalier, *Les Matières grasses*, 1910, 2001.

[3] E. Drabble, *Quart. Journ. Inst. Comm. Research in the Tropics*, 1907, ii. No. 5, 126.

[4] "Pericarp" denotes in this case the fleshy part of the fruit only, and not—as it should do in a strictly scientific sense—the stony shell of the kernels.

[5] *Les Matières grasses*, 1911, 2171.

Fat of Elais Guineensis

	Sub-species E. Nigrescens.					Sub-species E. Virescens.			
	Variety Communis.	Variety Vulgaris.		Variety Semper-nigra.	Variety Psifera.		Variety Repanda.	Variety Gracilinus.	Commercial Palm Oil.
Oil from pulp, per cent	41·0	43·0	47·0	52·0	50·0	60·0	63·0	52·0	.
Oil from whole fruit, per cent	22·0	21·0	29·0	16·0	42·0	56·0	32·0	30·0	.
Melting point of fat, °C	42·0	42·0	43·0	44·0	45·0	44·0	43·0	42·0	.
Specific gravity at melting point	0·882	0·881	0·888	0·892	0·891	0·889	0·884	0·889	0·945 (at 15° C.)
Saponification value	201·0	201·0	196·0	196·0	197·0	210·0	196·0	198·0	202·0
Reichert value	0·8	0·8	0·8	0·9	1·3	1·1	0·8	1·1	0·5
Iodine value	43·8	48·0	52·2	52·2	50·2	45·2	52·1	53·6	52·0
Hehner value	98·0	96·2	96·2	98·1	97·7	97·8	95·0	97·7	95·0
Melting point of fatty acids, °C	46·0	48·0	48·0	48·0	47·0	46·5	44·0	44·0	47·0

The Parliamentary returns made in 1845 of the palm oil imported from the West Coast of Africa are of historical interest and are given below :—

Palm Oil imported into United Kingdom

Year.					Cwts.
1790	.	.	.	.	2,599
1810				.	25,754
1830	.	.	.	.	. 213,467
1840	.	.	.	.	315,458

The bulk of palm oil is shipped to Liverpool. Smaller quantities go to Marseilles, Rotterdam, and Hamburg. The following tables give detailed statistics as far as they are available :—

Imported into the United Kingdom

Year.						Tons.
1900	.	.	.		.	43,025
1901		.	.			51,161
1902	.	.	.	.		57,311
1903	.	.	.			53,252
1904	.	.	.		.	51,021
1905	.	.	.	.		45,941
1906	.	.	.	.	.	54,061
1907	.	.	.	.		60,743
1908	.	.	.	.	.	62,694
1909				.	.	81,641
1910	.	.	.	.	.	87,050
1911	.	.	.	.		75,120
1912	.		.		.	78,365

Exported from the United Kingdom

Year.						Tons.
1900	.	.	.	.	.	31,219
1901	.	.	.			34,443
1902	.	.	.			39,041
1903	.	.	.			36,425
1904	.	.	.	.		35,920
1905	.	.	.	.	.	34,674
1906	.	.	.	.	.	33,771
1907	.	.	.		.	41,908
1908	.	.	.		.	43,704
1909			.	.	.	50,828
1910	.	.	.	.	.	60,131
1911	.	.	.	.	.	44,682
1912	.	.	.	.	.	46,086

Imports of Palm Oil into France and Marseilles

In tons (of 1000 kilogrammes)

| Year. | France. | | Marseilles |
	Imports	Exports	Imports.
1896	16,227	525	8,803
1897	11,820	235	6,732
1898	15,675	239	7,182
1899	17,759	388	12,624
1900	22,345	324	15,912
1901	17,760	72	10,351
1902	20,592	419	11,161
1903	18,109	364	12,236
1904	16,317	442	11,972
1905	17,263	441	13,203
1906	14,333	163	8,631
1907	16,087	291	12,029
1908	17,811	650	15,213
1909	17,765	1538	16,004
1910	16,088	2150	11,129
1911	17,991	1890	16,699

It is impossible to give the imports into Germany previous to 191 as up till then the imports of palm oil were included in the statistic data for solid fats. The German imports and exports for the yea 1911 and 1912 are given below :—

| | Imports from | | | Exports to | |
| | British West Africa. | Togo. | Liberia | Austria-Hungary. | Switzerland |
	Metric tons.	Metric tons.	Metric tons	Metric tons.	Metric tons.
1911	12,018	235	257	104	.
1912	12,667	258	662	24	30

In the trade the oils are classified as follows :—

1. *Soft oils*, notably Lagos, Calabar, Opobo, Bonny.
2. *Hard oils*, Congo, Niger, Oil River, Liberia, Gold Coast.
3. *Mixed oils* from the Gold Coast and Niger district.

Statistical details as to the quantities exported from the individua districts of West Africa are now being collected more carefully. A present only the following details are available :—

Sierra Leone

Year.						Value.
1901	.	.	.	.	.	£9,816
1902	.	.	.			13,544
1903	.	.	.	.		14,068
1904	.	.	.			16,245
1905	.	.	.		.	18,524
1906 (375,573 gallons)	.				.	27,745
1907 (615,997 gallons)						51,154
1908	.	.	.			37,676
1909	.	.	.		.	64,369
1910	.	.	.			64,410
1911	.	.	.			66,265
1912	.	.	.			67,878

Gold Coast

Year.				Gallons.	Value
1895	.		.	4,338,627	£231,415
1896	.	.	.	2,394,563	126,857
1897	.	.	.	2,021,716	107,737
1898	.			2,145,138	114,288
1899		.		3,323,919	183,204
1900	.	.	.	4,238,685	238,812
1901		.	.	3,146,390	178,171
1902	.	.	.	4,227,655	235,211
1903	.	.	.	2,589,591	145,896
1904	.	.	.	2,236,703	128,752
1905	.	.	.	1,598,272	88,359
1906	.	.	.	2,143,118	125,008
1907	.		.	1,867,945	119,468
1908	.		.	2,255,371	129,535
1909	.			2,007,296	120,978
1910	.	.	.	2,044,868	161,388

Ivory Coast

Year.						Kilos.
1901	.	.	.	.	.	5,113,644
1902	.	.	.	.	.	6,173,007
1903	.	.	.	.	.	4,863,561
1904	.	.	.	.	.	5,839,970
1905	.	.	.		.	3,270,578
1909	.	.	.	.	.	5,557,357

Lagos

Year.				Gallons.	Value.
1890	.	.	.	3,200,824	£190,657
1891	.	.	.	4,204,825	252,958
1892	.	.	.	2,458,260	137,743
1893	.	.	.	4,073,055	252,051
1894	.	.	.	3,393,533	187,928
1895	.	.	.	3,826,392	205,553
1896	.	.	.	3,154,333	159,150

Lagos (continued)

Year.				Gallons.	Value.
1897	.	.	.	1,858,968	£97,590
1898	.	.	.	1,889,939	97,337
1899	.	.	.	3,292,881	168,457
1900	.	.	.	2,977,926	190,165
1901	.	.	.	3,302,055	207,468
1903	.	.	.	. .	218,245
1904	.	.	.	.	219,114

Southern Nigeria [1] and Lagos

Year.					Value.
1905	.	.	.	.	£1,047,034
1906	.	.	.	.	1,122,671
1907					1,492,883
1908	.		.	.	1,235,241
1909	.				1,540,485
1910				.	2,140,894
1911					1,903,196
1912			.	.	1,910,980

In 1910 the export of palm oil from Togoland was 3,018,864 kilos, and in 1911, 3,964,596 kilos.

French Colonies

In tons (of 1000 kilogrammes)

Year	Senegal	French Guinea	Ivory Coast	Dahomey	French Congo.
1900	.	61	4340	8,929	112
1901		199	5114	11,290	116
1902		182	6173	12,676	170
1903		94	4863	6,961	98
1904	9	171	5840	8,368	152
1905	12	23	3270	5,537	159
1906		86	4856	6,378	91
1907		94	5662	7,835	
1908	223 kilos	169	5557	9,520	95
1909	955 ,,	48	6367	15,016	154 [2]
1910	1111 ,,	55	5955	14,628	130

[1] Earlier statistical data for Southern Nigeria, the Porto Novo transit lots included are —

Year.			Gallons.	Value
1900	.	.	12,741,585	£681,296
1901			15,894,404	813,478
1902			17,966,857	957,637
1903	.		15,192,135	847,954
1904	.		16,225,175	929,168
1905			14,157,384	868,028
1906			16,682,571	1,001,648
1907		.	18,392,581	1,313,912

[2] Including Gabon.

Palm oil has a somewhat sweetish taste; in its perfectly fresh state it is used as a culinary fat in the villages of the West Coast of Africa. Its odour is pleasant and resembles that of violets; this odour is not destroyed by bleaching with air at elevated temperatures, and persists even after the oil has been made into soap. In consequence of the very crude mode of producing palm oil, causing it to remain for a considerable time in contact with fermentable vegetable tissue, hydrolysis rapidly sets in, so that the oil on reaching the coast contains already a notable amount of free fatty acids. Palm oil when shipped from the coast has at least 10-12 per cent of free fatty acids. The process of hydrolysis, once begun, continues in the barrels during the voyage, and in consequence thereof commercial palm oils, on arriving at their destination, contain frequently from 20 to 50 per cent, and even more, of free fatty acids. In such palm oils free glycerol is found.[1] In old samples the hydrolysis may even reach completion, so that such palm oil practically consists of free fatty acids (*Lewko-witsch*). The progress of hydrolysis can be observed even in oils kept in glass bottles. Thus a sample of Drewin oil, which had originally the acid value 41·8, showed after six (summer) months the acid value 70·1. The hydrolysis of the oil contained in the fruit has been shown by *Dunstan* to be as follows :—

	Acid Value.
Oil from fresh fruits	8·4
Oil from fruits fermented 8 days	13·2
Oil from fruits fermented 6 weeks	103·7

The value of a palm oil in the markets depends on the care with which it has been prepared, as also on the particular locality from which it is derived. The " soft " oils are those containing a small quantity of free fatty acids, whereas the " hard " oils contain a large proportion of free fatty acids. It has been shown that the oil obtained from fruits which have been allowed to ferment is much " harder " than the oil produced from the fresh fruit.[2] The best " soft " oils come from Lagos and Dahomey. Next in quality are the River Oils (" medium " oils); whilst the lowest quality, the hardest oil, is represented by Congo oil.

The following table, due to *Y. de Schepper and Geitel*,[3] gives an indication as to the proportion of water, impurities, neutral fat, and the solidifying points of the insoluble fatty acids met with in commercial brands of palm oil :—

[1] Cp. Stenhouse, *Liebig's Annal.*, 1840 (36), 55.
[2] *Bull. Imp. Inst.*, 1913, 206.
[3] *Dingl. Polyt. Journ.*, 245, 295.

Kind of Oil.	Water.	Impurities	Solidifying Point of Fatty Acids	Neutral Fat
	Per cent	Per cent	°C.	Per cent
Congo . . .	0·78 0 95	0 35-0 7	15·90	16-23 0
Saltpond[1] . . .	3 5-12 5	0 9-1 7	46 20	15-25
Addah . . .	4 21	0 35	41·15	18·0
Appam . . .	3 60	0 596	45 0	25·0
Winnebah . .	6 73	1 375	15·6	20·0
Fernando Po . .	2·68	0 85	15 90	28
Brass . . .	3·05	2 00	15 1	35·5
New Calabar . .	3 82	0 86	15 0	40 0
Niger . . .	3·0	0 70	15 0	40 0 -17·0
Accra . . .	2 2-5·3	0 60	41 0	53-76
Benin . . .	2·03	0 20	45 0	59-74
Bonny . . .	3 0-6 5	1 2-3·1	41 5	41·0 88 5
Gr. Bassa . .	2·4-13·7	0 6-3	41 6	41-70·0
Cameroons . .	1·8-2 5	0·2-0 7	41 6	67-83
Cape Labon . .	3·6-6 5	0 7-1 5	41 0	55-69
Cape Palmas .	9 7	2 70	42·10	67
Half Jack-Jack .	1 9-4·2	0 7-1 24	39-41 3	55-77·0
Lagos . . .	0 5 1 3	0 3-0 6	45 0	58-68
Loando . . .	1·5-3 0	1 0 1 9	44 5	68-76
Old Calabar . .	1·3-1·6	0 3-0 8	44·5	76-83
Gold Coast . .	1 98	0 50	41 0	69
Sherboro . . .	2·6-7 0	0·3-1 2	42 0	60-74
Gaboon . . .	2·0-2 8	0·3-0·7	44 5	79-93 0
Benin Lagos . .	–	6·9		73·0
Benin Bonny . .	0·34	2·86	·–	75·65

It must of course be understood that the proportions of neutral fat depend greatly on the manner of preparing and keeping the oil.

The consistence of commercial palm oil varies from that of soft butter (Drewin [2]) to that of tallow (Congo oil). The colour also varies greatly, ranging, through all shades, from orange-yellow (Lagos) to dark dirty red (Congo).

The colouring matter of palm oil is not affected in the process of saponification by means of alkalis or lime; in the acid saponification process, however, it is destroyed. It is also slowly destroyed by exposure to air, more rapidly on heating or by bleaching with chemicals. The two latter processes are adopted in practice for preparing bleached palm oil.

Since palm oil, as pointed out already, is bleached by mere exposure to the atmosphere, hydrogen peroxide contained in the atmosphere is assumed to be the bleaching agent. This statement finds support in the fact that *Schonbein* obtained the hydrogen peroxide reaction with a specimen of palm oil. This explanation has been further elaborated by *Engler*.[3] The use of hydrogen peroxide for the bleaching of palm oil has been patented by *Vereinigte Chem. Werke*.[4]

Although palm oil can be bleached by means of ozone, yet several ozone processes examined by the author have hitherto not proved commercially successful, as the colour " reverts " in the palm oils so

[1] This is the cheapest hard oil.   [2] This is the cheapest soft oil.
[3] *Berichte*, 1900, 1101.   [4] German patent 214,937.

bleached. Bleaching by means of hot air, or by passing air through the heated oil, is capable of producing a tolerably white palm oil. The bleaching is carried out by blowing a current of air in a finely divided stream through the mass of oil, kept at a temperature exceeding $100°$ C. According to the kind of palm oil, the temperature must be raised up to $150°$ C. Heating the oil to temperatures of $250°$ C. does not produce a better result. In these processes the characteristic odour of palm oil is not destroyed.

The bleaching process most in vogue, and that giving the best results, is the bichromate process. The oil is freed from its gross impurities, and treated according to its quality with 1-3 per cent of potassium bichromate, and the requisite amount of hydrochloric acid. The dark "chrome" liquor is then carefully run off, and the oil is washed with water, at first with the assistance of a little mineral acid, until it is quite free from chromium and mineral acid.

Not all palm oils can be bleached successfully. Lagos and Old Calabar oils yield good results, but dirty coloured red oils, such as Congo oil, have hitherto withstood all attempts to bleach them.[1]

The chief constituents of palm oil are palmitin[2] and olein. The solid fatty acids consist, according to *Nördlinger*,[3] of 98 per cent of palmitic acid, 1 per cent of stearic, and 1 per cent of an acid described as a "heptadecylic" acid, $C_{17}H_{34}O_2$. This acid has, however, been shown by *Holde*[4] to represent a mixture in which an acid melting at 60-$65°$ C., and of the mean molecular weight 288 could be identified. Two specimens of palm oil, Bassa raw, and Lagos bleached, examined in the author's laboratory yielded 0·53 per cent and 0·72 per cent of stearic acid respectively. *Hazura and Grüssner* found among the liquid fatty acids small quantities of linolic acid, identified by the sativic acid yielded on oxidation. This is confirmed by the iodine values of the liquid fatty acids recorded in the table (p. 541).

Colour reactions proposed for the identification of palm oil are useless, and in any case unnecessary, since palm oil cannot easily be confounded with other fats or oils.[5] It may, however, be stated that some specimens of palm oil—Lagos oil and Old Calabar oil—give with sulphuric acid a colour reaction similar to that obtained with cod liver oil in chloroformic solution, although the blue is much fainter; other specimens do not give this blue colour, but turn red at once.[6]

Palm oil is, as a rule, not adulterated with other fats, and its commercial valuation embraces therefore the determination of water, of impurities (mostly sand, added fraudulently by negroes), and of the solidifying point. The proportion of water and sand together

[1] Cp. *Seifensieder Ztg.* 1913, 687, 724, 749, 769.
[2] Palmitic acid was discovered in palm oil by Fremy, *Liebig's Annal.*, 1840, 36, 50.
[3] *Zeitschr. f. angew. Chem.*, 1892, 110.   [4] *Berichte*, 1905, 1257.
[5] With regard to the detection of palm oil, when used as a colouring material for oils and fats, cp. Crampton and Simons, *Journ. Amer. Chem. Soc.*, 1905, 270. Small quantities (2-3 per cent) of palm oil used to be added to margarine ("oleomargarine") in the United States in order to give it a yellowish tint. As these colour tests appear to the author very uncertain, and moreover as the addition of palm oil to margarine is now forbidden by law, the reader must be referred to the original papers.
[6] Cp. Salkowski, *Zeitschr. f. analyt. Chem.*, 1887 (xxvi.), 569.

should not exceed 2 per cent; for any excess, allowance is usually made by the seller.

Palm oil is chiefly used in the soap[1] and candle industries.[2] In the latter industry it is valued *cæteris paribus* by its " titer." Being a non-drying oil, it is also employed in the tinplate industry, to preserve the surface of the heated iron sheet from oxidation until the moment ·of dipping into the bath of melted tin.

For the purpose of the tin industry " palm oil greases " are sold, consisting of palm oil adulterated with cotton seed oil and mineral oil of the specific gravity 0·905.

GAMBOGE BUTTER

French—*Graisse (Beurre) de Gamboge.*   German—*Gambogebutter.*
Italian—*Burro di Gamboga.*

Gamboge butter is the fat obtained from *Garcinia morella*, Desrouss, a tree common in the forests of Western India up to an altitude of 3500 feet; it is also frequently found in Ceylon. A variety of the fat, obtained from " Murga " seeds (*Garcinia ?*), is used for all cooking purposes like " ghee." A similar fat, from the seeds of the variety known as " Gurgi " (*Garcinia morella*), is used for lighting, cooking, and as a medicine for sprains and injuries (cp. also p. 598). The following characteristics are given by *D. Hooper*[3] : —

	Murga.	Gurgi.
Fat—		
Specific gravity at 50° C . . .	0 900	0·902
Melting point . .	37° C.	33·5° C.
Saponification value .	198·20	194·74
Iodine value	53·72	55·46
Reichert-Meissl value	0·69	0·62
Acid value	3·49	13·79
Fatty Acids—		
Insoluble fatty acids + unsaponifiable	94·89 per cent	95·20 per cent
Melting point	56° C.	55° C.
Iodine value	56·38	57·81

The insoluble fatty acids of the " Murga " butter consist chiefly of stearic acid (about 30 per cent) and oleic acid; only small quantities of palmitic acid are present. *Hooper* conjectures that the fatty acids consist chiefly of dioleo-stearin.

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[1] The negroes in the Togo district make a soap from palm oil and ashes obtained by burning banana leaves.

[2] First suggested for candle industry 1836 by Hempel and Blundel.

[3] *Journ. and Proceed. Asiatic Soc. of Bengal* (New Series), 1907, vol. iii. No. 5, 258.

AKEE OIL [1]

French—*Huile d'Akée*.　German—*Akeeöl*.　Italian—*Olio di akee*.

Akee oil is a yellow, buttery fat, stated to be obtained from the arillus of *Blighia sapida*, Kon., a tree indigenous to tropical West Africa (Guinea Coast). Its cultivation was introduced into Jamaica between 1794 and 1838.

The fatty acids distil unchanged under a pressure of 13 mm. at 220°-225° C. They consist approximately of 50 per cent of oleic acid and 50 per cent of solid saturated acids. The acid value of the sample examined was 20·1.

The oil appears to be very similar to palm oil.

Physical and Chemical Characteristics of Akee Oil

Specific Gravity	Solidifying Point	Melting Point	Saponification Value.	Iodine Value	Reichert-Meissl Value,
99°-100° (water 15·5 = 1)	°C.	°C.	Mgms. KOH	Per cent	cc. $\frac{1}{10}$ norm. KOH
0·857	20	25-35	191·6	49 1	0·9

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable	Specific Gravity,	Solidifying Point.	Melting Point	Saponification Value	Iodine Value.
Per cent.	99°-100° (water 15·5 = 1)	°C.	°C.	Mgms. KOH	Per cent
93	0·8365	40-38	42-16	207·7	58·4
					Liquid Fatty Acids.
					82·4

[1] Garsed, *Pharm. Journ.*, 1900, 691.

MACASSAR OIL, KUSUM OIL

French—*Huile de Macassar*.   German—*Macassarol*.
Italian—*Olio di Macassar*.

For tables of characteristics see p. 554.

Macassar oil is the fat from the seeds of " Paka " (" pacca " in Calcutta), *Schleicheria trijuga*, Willd. (the " Kusum " [1] tree of India, " Lac tree of Kosumba," " Ceylon Oak "), belonging to the *Sapindaceæ*.[2] The seeds consist of 40 per cent of shells and 60 per cent of kernels. The latter yield 70·5 per cent of a fat, which is known in India as " Kon oil," and in Celebes as " Ketjatkil oil "; known also in Cambodia as " Pongro oil."

According to a more recent examination, carried out by *J. H. Walker*, the kernels yield 60·4 per cent of oil, which is equivalent to 36·7 per cent of oil in the whole nuts.[3] Seeds from Cambodia examined by *Heckel*[4] consisted of 35 per cent of shells and 65 per cent of kernels. The whole seed yielded by extraction with carbon bisulphide 40·8 per cent of oil and the kernels 62·7 per cent.

The fat forms at the ordinary temperature a yellowish-white, buttery mass. It consists chiefly of the glycerides of lauric, palmitic, arachidic, and oleic acids, and contains also small quantities of acetic and butyric acids. The specimens examined by *Wijs*[5] yielded 45 per cent of solid and 55 per cent of liquid fatty acids. A very small proportion of hydrocyanic acid,[6] from 0·03 to 0·05 per cent (*Wijs*), seems to be characteristic of macassar oil. A sample examined in the author's laboratory had the acid value 35·13. Specimens examined by other observers gave acid values varying from 6·2 to 19·2. The amount of unsaponifiable matter in the specimen examined by *Wijs* was 3·12 per cent.

In the Indian villages Macassar oil is employed as an illuminant, and the freshly expressed oil is used for cooking purposes in the United Provinces, and as a hair oil in the dangs of Bombay. The oil is also largely used for medicinal purposes, thus : as a purgative in the United Provinces, as a prophylactic against cholera in the Thana division of Bombay, and also externally in massage for rheumatism, for removing itch and other forms of skin diseases.

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[1] This is the Hindustani name for the safflower plant, and perhaps refers to the colouring matter of the lac insect which often feeds upon the tree (D. Hooper, *Agricult. Ledger*, 1905, No. 1).

[2] The native name (in Celebes) of the seeds is Kusambi (Koesambie) nuts ; hence the alternative name *Cassumbium spinosum*. Other botanical names of the plant are *Stadmannia sideroxylon*, Bl., and *Melicocca trijuga*, Juss.

[3] *Agricult. Ledger*, 1905, No. 1.

[4] *Les Matières grasses*, 1910, 1922.

[5] *Zeitschr. f. phys. Chemie*, xxxi, (Jubelband) 255.

[6] Probably liberated by the action of an enzyme on a cyanogenetic glucoside.

Physical and Chemical Characteristics of Macassar Oil

Specific Gravity		Solidifying Point		Melting Point		Saponification Value		Iodine Value		Reichert-Meissl Value	
At 15° C	Observer	°C	Observer	°C	Observer	Mgrms KOH	Observer	Per cent	Observer	c.c. N/10 KOH	Observer
0·924	Italie	10	Gleuk	22	Italie	230	Italie	53	Italie	9	Wijs
0·924	Heckel			22·1	Wijs	221·5	Lewkowitsch	48·3	Lewkowitsch		
						215·3	Wijs[2]	69·1	Roelofsen		
								55	Wijs		

[1] By Crossley and Le Sueur's method.   [2] By cold saponification.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids ÷ Unsaponifiable		Solidifying Point		Melting Point		Neutralisation Value		Iodine Value	
Per cent	Observer	°C (Titer Test)	Observer	°C	Observer	Mgrms. KOH	Observer	Per cent	Observer
91·4	Italie	51·6-53·2	Lewkowitsch	54-55	Italie	191·2-192	Wijs	49·7-50·7	Lewkowitsch
91·5	Wijs								

Liquid Fatty Acids.

Iodine Value	
103·2	Wijs

SAWARRI FAT [1]

French—*Huile de noix de Souari.*   German—*Sawaributter.*
Italian—*Burro di noci di Souari.*

Sawarri fat is contained in the nuts from *Caryocar tomentosum,* Willd. (*Caryocar butyrosum,* Willd., *Caryocar nuciferum*),[2] imported occasionally from South America into this country as " butter nuts " from Demerara, where they are known under the name " Suari " or " Surahwa." The tree has been introduced into St. Vincent. The seeds contain 60 per cent of a fat which is colourless and possesses a pleasant, nutty taste. The free fatty acids in the specimen examined amounted to 2·4 per cent, calculated as oleic acid.

The solid fatty acids consist chiefly of palmitic acid. The liquid fatty acids contain besides oleic acid (identified by its oxidation product, dihydroxystearic acid) a hydroxylated acid which is readily converted into a lactone. The acetyl value of the liquid fatty acids was 14·03.

Physical and Chemical Characteristics of Sawarri Fat.

Specific Gravity at 40° C (water at 15°-1)	Solidifying Point °C	Melting Point °C	Saponification Value Mgrms KOH.	Iodine Value Per cent	Reichert Value c.c. ¹⁄₁₀ norm KOH
0·8981	29·23·3	29·5-35·5	199·51	49·5	0·65

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable Per cent.	Solidifying Point °C	Melting Point °C	Mean Molecular Weight	Iodine Value Per cent
96·91	47-46	48·3-50	272·8	51·5

MAFURA TALLOW [3]

French—*Suif (Beurre) de Mafura ; graisse de Mafouraire.*
German—*Mafuratalg.*   Italian—*Sego di Mafura.*

For tables of characteristics see p. 558.

Mafura tallow is contained in the seeds of (*Mafureira oleifera*) *Trichilia emetica,* Vahl. The fruits are small brown, ovoid nuts

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.,* 1890, 844 ; *Proceed. Chem. Soc.,* 1889, 69
[2] According to Semler, *Der Tropenpflanzer,* 1887, vol. ii. 449, the oil from this specimen of *Caryocar* is known as Pekeanut Oil.
[3] De Negri and Fabris, *Annali del Lab. Chim. delle Gabelle,* 1891-92, 271.

(about $\frac{3}{4}$ inch long and $\frac{1}{2}$ inch broad) covered with a thin brown shell, which is easily detachable by rubbing; about 1600 nuts weigh one pound. The kernels amount to 88 per cent and the shells to 12 per cent of the whole nuts. On extracting the nuts with ether 61 per cent of fat is obtained, whilst the kernels alone yield 68 per cent, and the shells alone 14 per cent.[1]

The production of this seed is on the increase, for whereas in 1911 57,000 kgs. were exported from Laurenzo Marques, in the first six months of 1913 the exports had risen to 2,000,000 kgs.

The fat has a dark yellowish colour which cannot readily be removed by bleaching; it is free from taste. Its odour recalls that of cacao butter.

Suzzi[2] examined seeds from Ghinda (Erythrea, Italian East Africa). The seeds are about 18 mm. long and 8 to 12 mm. broad. The weight of 1 litre of seeds is about 520 grms. The kernels are white, but rapidly become brown on drying. The shells contain 51·2 per cent, the kernels 64·4 per cent, and the entire nuts 60·5 per cent of fat. *Suzzi* examined separately the fat from the shells and that from the kernels with the results set out below :—

	Fat from the Shells expressed in the Cold	Fat from the Kernels expressed at 60° C.
Fat—		
Specific gravity	0·9192-0·9256 at 15° C.	0·857 at 100° C.
Solidifying point	4·3° C.	32-38° C.
Melting point	...	36-39° C
Saponification value	203·6	198
Iodine value	65	41
Fatty Acids -		
Solidifying point	43-42° C.	50·5-48·5° C.
Melting point	46-47° C	52-53·5° C.
Neutralisation value	201·2	205·8
Mean molecular weight	278·8	272·5

An examination of corresponding samples in the Imperial Institute [1] gave the following somewhat different results :—

	Fat from Shells.	Fat from Kernels.	Fat from entire Nuts.	Fat from Kernels.
Saponification value	209·7	200·3	240	241
Iodine value	71·6	52·6	55·8	47·8
Titer test (fatty acids)	45·4	53·2	..	.
Unsaponifiable matter, per cent	1·3	1·4	..	..

Two fats evidently corresponding to those examined by *Suzzi*, and prepared by the natives of Portuguese East Africa (where the

[1] *Bull. Imp. Inst.*, 1903, 27 ; 1908, 376.
[2] *I Semi oleosi e gli oli*, published for the Milan Exhibition, 1906, 36.

fruits are known under the native names *Umkuhlu, Mkhuklu, Marba, Marwa-Maawa, Gnande, Mafoureira, Mafura,* or *Mafurrera*), were examined by *Daniel and M'Crae.*[1] The mode of preparation is not stated, beyond the indication that on boiling the fruits (with water ?) a clear yellow oil—*mafura oil*—is skimmed off, which is used for cooking purposes, and that after the seeds are crushed *mafura tallow* is extracted. The latter is used by the natives for greasing the skin ; it is considered by the natives to be poisonous, but the toxic properties have not been confirmed by *Daniel and M'Crae.* In the following table the results of their examination are collated :—

	Mafura Oil.	Mafura Tallow.
Fat :—		
Specific gravity at 15/15° C.	0·931	...
,, ,, at 30/15° C.	0 920	0·909
,, ,, at 40/15° C	0·913	0 902
Melting point		29 5°-38° C.
Saponification value	202 5	201
Iodine value	66	43·5
Reichert-Wollny value	2·0	1·3
Saponification value of acetylated fat.	235	218
True acetyl value	36·5	16
Butyro-refractometer ; "degrees"		
,, ,, at 20° C. .	65 6	...
,, ,, at 30° C. .	60 1	...
,, ,, at 40° C. .	64 6	47 3
Unsaponifiable, per cent	0·8	1·2
Free fatty acids, ,,	8·9	14·7
Insoluble Fatty Acids		
Specific gravity at 92/15° C.	0·854	0·43
Solidifying point	44·2° C.	52·1° C.
Neutralisation value	201	204
Saponification value	206	205
Iodine value	68	46
Butyro-refractometer : "degrees"	37·2 at 50° C.	26·3 at 57° C.

"Mafura oil" does not give the *Halphen* test, and is optically inactive.

Villon's statement that it consists of 55 parts of olein and 45 parts of palmitin requires confirmation. The high melting point of the insoluble fatty acids would seem to render this fat especially suitable for the manufacture of soaps and candles.

The seeds of *Trichilia subcordata,* a tree growing in German East Africa yield 55·7 per cent of a fat having the following characteristics :—

Fat—
Solidifying point . . . . 30-24° C
Melting point . . . . 45° C.
Saponification value . . . 201·5
Iodine value . . . . 39·9
Acid value . . . . 39·6
Reichert-Meissl value . . . 3·3

[1] *Analyst,* 1908, 276.

Fatty Acids—

Solidifying point	.	.	.	51·5° C.
Melting point	.	.	.	54-55° C.
Iodine value	.	.	.	42·4

Fat from the seeds of Japanese medlar *Eriobotrya Japonica* examined by *G. Maderna* [1] had the following characteristics :—

	Fat obtained by Pressing.	By Extraction.
Specific gravity at 15° C.	0·967	...
Melting point, ° C.	49	48
Butyro-refractometer at 45° C.	75·5	76
Acid value	90·5	89·5
Saponification value	179·9	...
Iodine value	48·7	48
Reichert-Meissl value	5·4	...

The fatty acids had the neutralisation value 160 and the saponification value 173. The solid acids contained arachidic and palmitic acids.

Fat from *Litsaea Zeylanica*, which appears to be nearly related to tangkallak fat, is obtained from the seeds of a tree growing in the Nilgiri Hills, South India. The seeds yield 61 per cent of a yellowish fat. The following characteristics were ascertained by *D. Hooper* [2] in a specimen having the acid value 10.

Specific gravity at 40° C.	.	.	0 9317
Melting point	.	.	40
Saponification value			244 7
Iodine value	.	.	46·5
Fatty acids + unsaponifiable, per cent		.	91·3 [3]
Melting point of fatty acids, ° C.	.	.	40

The oil is used medicinally as also for candle-making.

Physical and Chemical Characteristics of Mafura Tallow

	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.	Observer.
	° C.	° C.	Mgrms. KOH.	Per cent.	
I. Prepared in the Laboratory	33-25	35-41	200 08	44 85	De Negri and Fabris
„ from the entire nuts	30-25	35-40	200 2	47 5	Suzzi
II. Commercial	37-30	35 5-42	220 16	46 14	De Negri and Fabris

[1] *Boll. Chim. Farm.*, 1910, 713.

[2] *Annual Report Indian Museum*, 1908, 10.

[3] In view of the fact that this fat contains large quantities of lauric acid, the percentage found would depend on the amount of water used for washing the fatty acids (see Vol. 1. p. 155).

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Solidifying Point.	Melting Point.	Neutralisation Value.	Saponification Value.	Iodine Value.	Observer.
	° C.	° C.	Mgrms. KOH.	Mgrms KOH.	Per cent.	
1.	47·44	51·54	..	..	46·92	De Negri and Fabris
	49·46 49·5 (Titer test)	51·54	194·3	197		Suzzi
11.	48·44	52·55	..	..	48·19	De Negri and Fabris

Myristica Group

The members of this group belong to the family of *Myristicaceæ*, and are characterised by a large proportion of myristin, hence they have high saponification values. Some of these fats, like ochoco fat, consist almost entirely of myristin. The following fats arranged, as far as is possible at present, in the order of their iodine values, include the better known members of this group :—

     (*a*) Nutmeg butter, Mace butter.
     (*b*) Papua nutmeg butter.
     (*c*) Myristica malabarica.
     (*d*) Kombo fat.
     (*e*) Fat from Myristica canarica
     (*f*) Fat from Myristica guatemalensis—virola fat.
     (*g*) Fat from myristica surinamensis.
     (*h*) Ucuhuba fat, Urucaba fat.
     (*i*) Ochoco fat.

Iriya oil,[1] the oil obtained from *Myristica iriya*, an evergreen shrub indigenous to Ceylon, appears to be an ethereal oil, as it is obtained from the bark. This oil was exhibited at the Paris Exhibition of 1900, and is stated to be applied by the natives as a remedy in cutaneous diseases.

[1] *Bull. Imp. Inst.*, 1901.

(a) NUTMEG BUTTER, MACE BUTTER

French—*Beurre de muscade.*   German—*Muskatbutter.*
Italian—*Burro di noce moscata.*

For tables of characteristics see pp. 563, 564.

Nutmeg butter is obtained from the seeds of *Myristica officinalis*, L. (*M. moschata*, Thunb., *M. fragrans*, Houtt.), a tree growing wild on the islands of the Indian Archipelago, notably Celebes, Sumatra, Java, Molucca, and the Banda Islands. The tree is now cultivated in these islands. By far the largest quantity of nutmegs imported into Europe comes from the Banda Islands. The tree, or at least varieties thereof, is also cultivated in the West Indies, Brazil, and Guiana. The pericarp of the seed yields the arillus (mace) which is used in pharmacy, as a condiment for culinary purposes, and for the preparation of the ethereal oil contained in it. Formerly the small, as also the worm-eaten, rejected nuts which could not be exported, were worked up for mace butter on the islands of the Indian Archipelago. The nuts were ground to a coarse meal, filled into sacks, and steamed for about six hours over boiling-pots. The sacks were then subjected to pressure. The butter so obtained represented a brownish mass. This was exported in the shape of bars (resembling soap bars) wrapped in cocoa nut tree leaves (hence these bars were termed " soap of Banda "). At present mace butter is chiefly obtained in European works (Holland), where the nuts are powdered and expressed in the hot. The fat is also prepared in small quantities by extraction with petroleum ether,[1] or common ether, in pharmaceutical laboratories.

The world's annual production of nutmegs does not exceed 1500 tons. Only a small quantity thereof is used in the manufacture of nutmeg butter, so that the price of the fat is somewhat high. The seeds contain 38-40 per cent of fat. Nutmeg butter has the consistence of soft tallow, is of whitish colour, and has the strong taste and odour of nutmegs.

The commercial fat varies considerably in composition (see table below). It contains from 4 to 10 per cent of an ethereal oil[2] (hence the low saponification value), and consists chiefly of trimyristin, in addition to a liquid fat and free fatty acids.

Cold alcohol dissolves the liquid fat, the free acids, and the ethereal oil (unsaponifiable), leaving about 45 per cent undissolved. The undissolved portion yields on crystallisation from ether, pure trimyristin, melting at 55° C.

Boiling alcohol dissolves nutmeg butter almost completely. The solubility in alcohol is not only due to the high percentage of free fatty acids contained in the commercial samples, but also to the ready solubility of myristin itself in alcohol.

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[1] The seeds contain 38 to 40 per cent of fat, but the yield obtained by expression hardly reaches 30 per cent.

[2] An exhaustive examination of the ethereal oil has been made by F. B. Power and A. H. Salway, *Journ. Chem. Soc.*, 1907, 2037.

The following table contains a few characteristics ascertained by *Dieterich*; the first five samples were prepared by extracting nutmegs with ether:—

No. of Sample.	Specific Gravity at 15° C.	Melting Point, °C.	Acid Value.	Saponification Value.	Iodine Value.	Solubility in Parts of Boiling Alcohol
1	...	...	22·4	156·8	...	...
2	...	...	22·4	159 6	...	...
3	0·996	51	22·4	154 0	...	15
4	·	...	22 4	156 8	...	...
5	·		22 1	156 8	. .	
6	0·945	42	39 2	151·2	...	12
7	0 957	45	33·6	140 0		12
8	0 966	48	44·8	134 0		10
9	..	38·5-39	17 25	178 25	45·32	·
10	...	42	19·60	173 1 5	42·71	
11	...	43	18 67	172 2	40·14	·
12	·	42 5-43	18·67	171 51	41 38	
13	...	39	21·93	175 95	52 01	
14	...	38·5-39	22 80	178 67	48 60	...

The following are the results of an examination of commercial samples of nutmeg butter by *Spaeth*:- -

Origin.	Melting Point, °C.	Saponification Value.	Iodine Value	Reichert-Meissl Value	Refractive Index. Butyro refractometer at 40° C "Degrees."
Banda	25-26	170-173	77·8-80·8	4·1-4·2	76-82
Bombay	31-31·5	189 4-191·4	50·1-53·5	1·1-1·1	48-49 [1]
Monado	25·5	169 1	76·9-77 3	...	74-74·5
Penang	26	171 8-172·4	75 6-76·1	·	81·5-85
Macassar	25-25·5	171·8-172 4	75 6-76·1	. .	78 5
Zanzibar	25·5-26	169·9-170 5	76·2-77	...	77·5

The discrepancies in the iodine values may perhaps be due to the varying quantities of ethereal oil. An experiment carried out in the author's laboratory, however, did not confirm this view, as a sample of genuine nutmeg butter of the iodine value 59·3 showed, after being freed from its ethereal oil by a current of steam, the iodine value 58·3.

From recent experiments made by *Fabris and Settimj* [2] it would appear that either the essential oil had not been driven off completely in this experiment or that there are present in crude nutmeg butter other foreign substances which are not readily volatilised. *Fabris and Settimj* digested crude nutmeg butter *obtained by extraction with ether* with 95 per cent alcohol at a low temperature (not exceeding

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[1] This fat is derived from *Myristica malabarica*, Lam. (p. 565) and should therefore not have been included by *Spaeth* in the above given table. (Private communication to the author from D. Hooper, Indian Museum, Calcutta.)

[2] *Atti del VI. Congresso internaz. di chimica applicata*, Roma, 1907, v. 756.

5° C.), and thus resolved the crude nutmeg butter (the characteristics
of which are given in the tables p. 563) into an alcohol-insoluble, almost
white and odourless fat, and an oily, reddish-brown fat having a very
pronounced smell of mace. The latter portion formed about 6 per
cent of the crude fat. Some characteristics of the alcohol-insoluble
and alcohol-soluble portions were ascertained by *Fabris and Settimj*;
it would appear that the alcohol-insoluble portion is practically pure
myristin.

	Fat Insoluble in Alcohol at 5° C.	Oil Soluble in Alcohol at 5° C.
Melting point	55 to 56° C.	...
Saponification value . . .	226·1	46·8
Iodine value	7·0	114·3
Butyro-refractometer ; " degrees " . .	35 at 50° C.	93·5 at 90° C.

Nutmeg butter is frequently substituted by fats from other species
of *Myristica*. Recently the demand for mace butter has caused the
importation of nuts from *Myristica argentea*, Warb., the so-called
Papua nutmeg, growing wild in Dutch New Guinea (see below). It
has been stated that commercial mace butter is frequently nothing
else but Papua nutmeg butter (see *b*).

Adulteration with waxes or unsaponifiable (mineral) waxes can
be easily detected.

In the East nutmeg butter serves for medicinal purposes.[1] In
Europe the butter is given in the official pharmacopœias as *Oleum
myristicæ*; it is used as a basis for ointments, etc.

The examination of a genuine nutmeg butter, obtained by express-
ing genuine Ceylon nutmegs, was recently undertaken by *Power and
Salway*.[2] The crushed nutmegs were subjected to a pressure of 4000
lbs. per square inch, at a temperature ranging between 45° and 75° C.
for eight hours, and were allowed to remain under pressure for about
twelve hours, during which time the temperature gradually fell. The
yield amounted to 26·6 per cent. The same raw material yielded on
extraction with ether 42·9 per cent of fat.

The following table contains some characteristics of (1) the ex-
pressed fat, (2) the fat extracted by ether, (3) the expressed fat freed
from essential oil by a current of steam, and (4) the total fatty acids :—

	Expressed Fat.	Fat extracted by Ether.	Expressed Fat free from Essential Oil.	Total Fatty Acids.
Specific gravity 50/50° C. . .	0·9399	0·9337	0·9443	0·9012
Melting point	48° C.	50° C	49° C.	49° C.
Saponification value . .	174·6..	180·5	199·6	
Iodine value	57·8	45·7	35·7	23·1
Acid value	11·2	12·9	14·0	218·3

[1] Krasser, *Chem. Revue*, 1897, 331.   [2] *Journ. Chem. Soc.*, 1908, 1653.

Physical and Chemical Characteristics of Nutmeg Butter

Specific Gravity		Solidifying Point		Melting Point		Saponification Value	
At °C	Observer	°C.	Observer.	°C	Observer	Mgrms. KOH.	Observer.
15	Dieterich	41-42	Rudorff	47-48	Rudorff	154-159·6	Dieterich
15	Fabris and Settimj	Turbid at 33 rising to 41·5-44	Wimmel	43·5-44	Wimmel	153·53-161	,,
100	Allen			51	Dieterich	169·1-191·4	Spaeth
98·99 (water 15·5=1)				42	,,		
	0·840			45	,,		
	0·898			48	,,		
		39-40	F. and S.	38·5-43			
				49-50	F. and S.		

Specific Gravity values: 0·945-0·996; 0·9·98; 0·840; 0·898

Physical and Chemical Characteristics of Nutmeg Butter—continued

Iodine Value		Reichert-Meissl Value.		Refractive Index		Maumene Test.	
Per cent.	Observer.	c.c. N/10 norm KOH.	Observer	(nD at 40° C	Observer	°C.	Observer.
40 1-52 0	Dieterich	1-4 2	Spaeth	1·1704	Utz	39	F. and S.
59·3	Lewkowitsch	2·1	F. and S.				
50 1-50 8	Spaeth			Butyro-refractometer			
48 8-65 1¹	Wijs			('Degrees.' Observer			
59 1-85 7²	,,			At 40° C. 67·0 Utz			
				At 50° C. 61 F. and S.			
				55 ,,			

¹ Oils expressed in Europe.   ² Indian oils.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Iodine Value.	
Per cent.	Observer.	° C.	Observer.	° C	Observer	Per cent.	Observer.
82·5 (?)	F. and S.	40 44·45	Hubl F. and S.	42·5 48·49	Hubl F. and S.	31·6	F. and S.
						Liquid Fatty Acids.	
		Titer Test.				93·5	F. and S.
		35·5· 35·95	Lewko- witsch				

The results of the investigation are summarised in the following table :—

Essential oil	12·5 per cent
Trimyristin	73·0 ,,
Oleic acid, as glyceride	3·0 ,,
Linolenic acid, as glyceride	0·5 ,,
Formic, acetic, and cerotic acids (very small amounts) .	
Unsaponifiable matter	8·5 ,,
Resinous material	2·0 ,,
	99·5 per cent

The unsaponifiable matter consisted of a substance of the formula $C_{18}H_{22}O_5$ (amounting to about 5 per cent of the expressed oil), some myristicin, $C_{11}H_{12}O_3$,[1] and a very small amount of an alcohol, $C_{20}H_{34}O$, melting at 134°-135° C. This alcohol is described as a " phytosterol " ; it differs from the ordinary phytosterol (sitosterol) (Vol. I. Chap. III.) by its different chemical composition, although it has the same melting point.

In addition to the *Myristica* species enumerated (pp. 559, 570) the following other members of the " Myristica Group " are described by *D. Hooper* [2] :—*Myristica malabarica*, *M. canarica*, *M. guatemalensis*, *M. laurifolia.*

(b) PAPUA NUTMEG BUTTER

French—*Beurre de muscade de Papua*
(" Macassar nutmeg butter ").

" Papua nutmeg butter," the fat from *Myristica argentea*, Warb., contains no ethereal oil, but is said to have the same characteristics as the fat from *Myristica officinalis* (see above).

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[1] Power and Salway, *Journ. Chem. Soc.*, 1907, 2037.
[2] *Agricult. Ledger*, 1907, No. 3.

(c) FAT FROM MYRISTICA MALABARICA

The seeds of *M. malabarica*, a tall evergreen tree growing in the forests of Konkan, Kanara, Malabar, and Travancore, are sold in Bombay as "kaiphal." The seeds contain 32 per cent of shells, and yield 40·76 per cent of fat and resins. The mace of the Bombay seeds differs entirely from that of the genuine mace from the official nutmeg. The mace of *M. malabarica* yields 63·26 per cent of fats and resins. The fat from the kernels of this species differs completely from the fat from *M. officinalis*. The characteristics of a Bombay fat (from *M. malabarica*) are given on p. 561, in the table due to *Spaeth*, and it will be observed that they differ entirely from those of the fat from *Myristica officinalis*.

(d) KOMBO FAT, KOMBO BUTTER

French—*Beurre de kombo, beurre de mutage.*

This fat is obtained from the seeds of *Myristica angolensis*, Welw., which are known in the Jebu-Ode district of Southern Nigeria by the name "Acoomoo."[1] In the Gold Coast Colony the seeds are known under the native name "Ote seeds."[2] In the Gaboon this oil is known as *beurre de Kombo*,[3] in Angola as *beurre de Mutage* or *beurre d'Ikoum* (Panouin). The seeds are described by *Warburg* as being obtained from *Pycnanthus Kombo* (Baillon), Warb. This latter tree is widely distributed in the Gaboon (where it is known as *arbre à suif du Gabon*), in the Congo, and Angola. The seed, after being freed from the arillus, but still retaining the shell, gave by extraction with carbon bisulphide 15·5 per cent of fat; the endosperm alone yields 56 per cent of a fat melting at 51° C., and solidifying at 49° C. The fat has a pleasant aromatic smell, but on standing is said to develop the odour of trimethylamine.

Specimens of fruits received by the Imperial Institute[4] from Northern Nigeria were of the size of a small, oval plum, weighing in the dry state about 4 grms. The fruit breaks up easily into two thick, hard pieces of husk, and an inner nut, covered with a false arillus. The seeds are frequently mistaken for nutmegs but they contain no ethereal oil.

The nut has a very thin shell which can be easily removed from the contained kernel. The ground kernels yielded on extraction with light petroleum ether 54 per cent of a hard fat, having the following characteristics : —

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[1] E. Drabble, *Quart. Journ. Inst. of Comm. Research in the Tropics* (Liverpool University), 1907, vol. ii, No, 5, 132.

[2] Catalogue of Exhibits of the Gold Coast Colony, Franco-British Exhibition, 1908.

[3] Heckel, *Les Graines grasses nouvelles ou peu connues des colonies françaises*, p. 105.

[4] *Bull. Imp. Inst.*, 1908, 378.

	Crude Fat.	Refined Fat.
Specific gravity at 99° C. (water at 15° C.=1)	0·887	...
Acid value	26 5	nil
Saponification value . . .	255 0	183·0
Iodine value	65·4	33·7
Insoluble fatty acids+unsaponifiable	90 9	...
Titer test	37	37·6

The very great difference in the iodine values between the crude and refined fats is not readily explainable.

The " Mace " yielded to solvents 57·04 per cent of an oil which develops a deep violet colour on treatment with alkalis. The oil gave the following numbers :—

Specific gravity at 99° C. (water 15° C.=1) .	0·866
Saponification value . . .	214
Iodine value . . .	77·45
Insoluble acids + unsaponifiable, per cent	91·2
Titer test (fatty acids) . . .	35° C.
The specimen had the acid value	40·7

(c) FAT FROM MYRISTICA CANARICA

The seeds from *Myristica canarica* have been occasionally imported into this country under the name " Oil Nuts " from Africa and South America. In India the seeds are derived from the " Candle-nut tree," growing on the Western Ghats, from the Konkan southwards.

The entire seeds yield 49·4 per cent of fat ; the mace 54·6 per cent of fat ; the kernels separated from the shells furnish 64·76 per cent of fat. The fat was light brown and crystalline, and gave in the cold with strong sulphuric acid a carmine-red colour.

The following characteristics were ascertained by *Hooper* :—

Fat—		
Melting point . .		37·5° C.
Saponification value . . .		215·02
Iodine value		26·64
Acid value		37·08
Fatty Acids—		
Insoluble acids + unsaponifiable .		92 per cent
Melting point		41° C.
Neutralisation value . . .		217·53

The solid fatty acid was separated by means of the lead-salt-ether method and was found to consist of myristic acid ; the proportion of myristic acid was found to be 70·8 per cent.

(*f*) FAT FROM MYRISTICA GUATEMALENSIS, VIROLA FAT

The seeds of *Virola fat*, from *Virola venezuelensis*, Warb., known in Venezuela by the local name " cuajo," contain, like the seeds from *Myristica moschata*, besides the fatty oil, an ethereal oil. The seeds yield 47·5 per cent of a brown fat, from which pure myristin of the melting point 54°-55° C. can be obtained by crystallising twice from ether (cp. Vol. I. Chap. 1.). *Virola guatemalensis* (Warb.), " African oil nuts," yield an oil of the iodine value 13·8. This is possibly identical with the oil from the nuts of *Virola surinamensis*. The shell forms 17 per cent of the seed; the kernels yield 74·7 per cent of a light brown fat, for which *Grimme* [1] ascertained the following characteristics :—

Fat—

Specific gravity at 50° C.	0·8996
Solidifying point, ° C.	44·5
Melting point, ° C.	47·0
Saponification value	221·5
Iodine value	12·4
Acid value	19·1
Refractive index at 40° C.	1·4541

Fatty Acids—

Insoluble acids + unsaponifiable, per cent	95·18
Unsaponifiable, per cent	0·86
Solidifying point, ° C.	39·5
Melting point, ° C.	43·0
Iodine value	12·9
Mean molecular weight	253·2
Refractive Index at 45° C.	1·4482

(*g*) FAT FROM MYRISTICA SURINAMENSIS

This fat is obtained from the " oil nuts," the seeds of *Myristica surinamensis*, *Virola surinamensis*, Warb. It has a crystalline structure, melts at 45° C. (*Reimer and Will.*),[2] and appears to have a chemical composition similar to that of ucuhuba fat. A specimen of crude commercial fat contained 87 per cent of triglycerides, 6·5 per cent of free myristic acid, and a caoutchouc-like (resinous) substance. To the presence of the last-named substance must be ascribed the fact that the crude fat is not completely soluble in petroleum ether or in boiling alcohol. The amount of insoluble fatty acids + unsaponifiable found by *Valenta* as 93·4 per cent includes, of course, the resinous substance. Probably identical with this is the seed from *Virola guatemalensis*, cp. p. 567, examined by *Grimme*. The seeds consisted of 14·6 per cent shell and 85·4 per cent of kernels. The kernels yielded 60·7 per cent of a light brown crystalline fat which had the following characteristics :—

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[1] *Chem. Revue*, 1910, 233 ; 263.   [2] *Berichte*, 1888, 2011.

Fat—

Specific gravity at 50° C.	0·9005
Solidifying point, ° C.	38·5
Melting point, ° C.	41·0
Saponification value	244·0
Iodine value	13·8
Acid value . . ' . . .	27·9
Refractive index at 50° C. . . .	1·4539

Fatty Acids—

Insoluble acids + unsaponifiable, per cent . .	94·83
Unsaponifiable matter, per cent . . .	1·13
Solidifying point, ° C.	36·8
Melting point, ° C.	38·0
Iodine value . . + . .	15·6
Mean molecular weight	246·5
Refractive index at 50° C. . . .	1·4486

(*h*) UCUHUBA FAT, URUCABA FAT, BICUHYBA FAT [1]

French—*Gruisse d'Ucuhuba, Suif du Muscadier brasilien.*
German—*Ucuhubafett, Urucabafett.*
Italian—*Sego di ucuhuba.*

Ucuhuba fat is obtained from the nuts of *Virola* (Myristica) *bicuhyba*, Humb. It is stated that the fat from *Virola bicuhyba* is usually mixed in Brazil with that of *Myristica officinalis.* Owing to the crude method employed in its preparation, the fat as brought into the market is yellowish brown, and has an aromatic odour (due to a small quantity of an ethereal oil), recalling that of cocoa nut oil.

Ucuhuba fat consists of myristin and olein (10·5 per cent), small quantities of an ethereal oil, of a resinous substance, and of a wax-like compound. The resinous substance is soluble in ether, hot alcohol, petroleum ether (?), and chloroform.

The sample examined by *Valenta* contained 8·8 per cent of free fatty acids. A sample examined by the author contained 3·15 per cent of resinous matter and 3·05 per cent of unsaponifiable matter.

Physical and Chemical Characteristics of Ucuhuba Fat

Specific Gravity.		Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Observer.
At ° C.		° C.	° C.	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	
..	..	..	39	219·220	9·5	..	Valenta [2]
..	..	32·32·5	42·5·43	..	..	..	Nördlinger [3]
$\frac{100}{100}$	0·9127⎱						
$\frac{100}{15}$	0·8715⎰	..	35·44·7	218·8	18·5	2·68	Lewkowitsch

[1] French patent 394,362 ; English patent 19,511, 1908 ; Italian patent 292/235/97945.
[2] *Journ. Soc. Chem. Ind.,* 1889, 202.   [3] *Berichte,* 1888, 2617.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids +Unsaponifiable.	Melting Point.	
Per cent.	° C.	Observer.
93·4	46	Valenta
..	42·5-43	Nördlinger
89·37	..	Lewkowitsch

(i) OCHOCO FAT [1]

French—*Beurre d'Ochoco.* German—*Ochocofett.*

Ochoco fat is contained in the seeds of *Scyphocephalium ochocoa*, War., a tree indigenous to the west coast of Africa. From a description published by *Pierre* [2] it appears that the nuts have no arillus and that they are non-dehiscent. He therefore looked upon the plant as representing a new genus of Myristicaceæ, and named the tree *Ochocoa gabonii*. Warburg,[3] in 1895, described the tree as *Scyphocephalium chrysothrix*, and later in 1897 as *Scyphocephalium ochocoa*.[4] The statement he made in 1895, viz. that the nuts had an arillus and are dehiscent, was corrected later on,[4] in so far that the question as to whether the nuts were possessed of an arillus or not was left open. A very large number of nuts examined some years ago by *Heckel*,[5] as also those submitted to the author, showed no sign of an arillus, and hence would not yield ethereal oil.

The specimens examined by the author were identified by the Kew authorities as the kernels of *Scyphocephalium ochocoa*. The average weight of the kernels is 10 grms. ; the smallest weighing 5 grms. and the largest 12·5 grms. The kernels together with the thin husks surrounding the endocarp yield 58·8 per cent of fat. By whatever process the fat is prepared, a dark brown colouring matter is at the same time extracted, which is so tenaciously retained by the fat, that the author has hitherto been unable to remove it. Similar difficulties were met with by *Heckel* and his collaborators. This dark colouring matter is not only contained in the husks but also in the membranous extension of the husk (spermoderm) which passes through the whole of the endosperm, in the form of irregular lamellæ radiating from the *chalaza*. As the examination of the dark fat offered some difficulties, the only way to obtain a fat free from colouring matter

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[1] Lewkowitsch, *Analyst*, 1908, 313.
[2] *Bull. de la Soc. linnéenne de Paris*, 1898, No. 5. *Séance du premier mai*, 1896.
[3] " Identificierung der sogenannten Ochoconusse aus Gabun mit Scyphocephalium einer neuen Muskatnuss-Gattung," *Notizblatt des Königlich. Bot. Gart.* Berlin, 1895.
[4] Warburg, "Monographie der Myristicaceen, *Acta Leopoldina*, Halle a/S. lxvm., 1897.
[5] *Les Graines grasses nouvelles ou peu connues des colonies françaises*, Paris, 1902.

was to cut out the white endosperm carefully by hand. The amount of endosperm so obtained formed 84·7 per cent of the kernels. These 84·7 per cent contained 69·4 per cent of fat.

The white endosperm, on being extracted in the usual manner, yielded a perfectly white fat of the acid value 1·42, which gave the following characteristics :—

Fat—

Specific gravity at 60° C. (water at 4°=1) .	0 8899
Melting point, ° C.	45·48
Saponification value	238·5
Iodine value	1·72
Reichert-Meissl value . . .	0·65
Insoluble volatile acids required . .	4·00c. c. decinorm. KOH.
Unsaponifiable matter, per cent . .	0·37

Fatty Acids—

Mean molecular weight of the fatty acids, freed from unsaponifiable matter .	221·9
Melting point (capillary tube), ° C. .	47·2
Iodine value	1·47

These numbers lie so near to those yielded by myristin that the fat may be considered as consisting of practically pure myristin, or about 98 per cent of myristin and about 2 per cent of olein. The mixed fatty acids gave on separation by means of the lead-salt-ether method 12·82 per cent of acids, the lead salts of which were dissolved by ether. The acids obtained from these lead salts were, however, solid, melted at 31·7-32·2° C. (in a capillary tube), and absorbed no more than 9·9 per cent of iodine.

The mean molecular weight of the insoluble volatile acids was found to be 227·3 (myristic acid = 228); they melted at 43·3-48·9° C. The mixed fatty acids lost by washing with a considerable quantity of boiling water were only 1·5 per cent. This shows that the acids consist practically of pure myristic acid, and inferentially that ochoco fat is free from laurin.

The natives apply the name " Ochoco " indiscriminately to several edible fruits, such as the fruits from *Lophira alata* (see " Niam Fat "), etc.

OTOBA FAT

Otoba fat, commercially known also as otoba wax, is the fat from *Myristica otoba*, Humb. and Bonp.

The otoba fat, which is known as American mace butter, is obtained in New Granada by pressing the seeds. In its fresh state it has a pleasant aromatic odour, like mace butter, but in the melted state it has an unpleasant smell. According to *Uricœchea* [1] the fat consists of myristin, olein, and a substance termed by him *otobit*. This sub-

[1] *Liebig's Annal.*, 1854 (91), 369.

stance is stated to crystallise in large prisms of melting point 133° C. (sitosterol ?). ·

FAT FROM VIROLA SEBIFERA

This fat is obtained by boiling the fruit from *Virola sebifera*, Aubl., with water. It forms a yellowish tallow-like mass, of slight ethereal odour, having the specific gravity 0·995 at 15° C., and melting at 45° C. The fat is stated to consist chiefly of myristin and olein, and is used commercially in Guiana in the manufacture of soaps and candles.

OCUBA FAT

The fat from *Myristica ocuba*, Humb. and Bonp., commercially known as ocuba wax, is obtained from the fruits of a shrub similar to our hazel nut trees. The nuts are surrounded by a thick skin, which yields on extraction with water a pink colouring matter—ocuba red. The seeds yield 20-22 per cent of " ocuba wax."

This fat is a commercial article in Belem, the capital of the province Para in Brazil, and is used there as a candle-making material. An exhaustive examination of this fat has not been made yet. The specific gravity is stated by some writers as 0·920 at 15° C., and its melting point is given as 39°-40° C. These data render it extremely unlikely that " ocuba wax " is chemically speaking a wax ; hence it is classed by the author amongst fats.

FAT FROM VIROLA MICHELI

This fat is obtained from the nuts of *Virola Micheli*, Heckel,[1] a tree occurring in French Guiana. The arillus yields by extraction with carbon bisulphide 47·1 per cent of a mixture of ethereal oil and fat. The endosperm gave 65·41 per cent (51·25 per cent of the total seed) of a solid white fat which must have contained considerable quantities of foreign substances, including ethereal oil, as the specific gravity is stated by *Heckel* to be 1·043 at 15° C.

FAT FROM STAUDTIA KAMERUNENSIS

The seeds of *Staudtia Kamerunensis*, Warb.,[2] freed from the arillus, yield 31·7 per cent of solid fat of a yellow colour, and an aromatic taste and odour. The insoluble fatty acids solidify at 39·2° C., and are stated to consist of myristic and oleic acids.

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[1] *Les Graines grasses nouvelles ou peu connues des colonies françaises*, p. 118.
[2] *Ibid.* p. 111

PHULWARA BUTTER, INDIAN BUTTER

French—*Beurre de Fulware (Ghé, Ghee)*. German—*Fulwabuter*, *Phulwarabutter*. Italian—*Burro di Fulwara ; burro di ghee*.

For table of characteristics see p. 573.

This fat is expressed from the seeds of *Bassia (Illipé) butyracea*, Roxb., the Indian "butter tree" (known locally under the names "Phulvara," "Churi," "Yel"), indigenous to the Himalayas. It must not be confounded with Mowrah seed oil nor Mahua butter. The seeds contain 50-52 per cent of fat, which has the consistence of lard and is stated to keep well, even in India, without becoming rancid.

The specimen examined by *Crossley and Le Sueur* had the acid value 16·44. No stearic acid could be detected in the fatty acids[1]

Phulwara butter is one of the most important food-stuffs amongst the natives of the North-West Provinces, on account of its pleasant odour and agreeable taste. The butter is also highly valued as an ointment, when properly perfumed ; it is frequently adulterated in India with kokum butter and mahua butter.

[1] Menon, *Journ Soc. Chem. Ind.*, 1910, 1428.

Physical and Chemical Characteristics of Phulwara Butter

Specific Gravity at 100°C. (water 100°=1).	Melting Point. °C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent	Reichert-Meissl Value. c.c. $\frac{1}{10}$ norm. KOH.	Insoluble Acids + Un-saponifiable Per cent	Unsaponifiable Matter Per cent.	Refractive Index at 40°C. Butyro-refractometer. "Degrees."	Viscosity Seconds at 140°F.	Observer.
0·8970	39	190 8	42 12	0 44	94 86	..	48·2	110·4	Crossley and Le Sueur
0·8924	43·51	194 6	41 2	1 25	95 1	2·20	44 0	..	Menon [1]

[1] Determined in the author's laboratory.

SURIN FAT [1]

French—*Huile de Surin.*   German—*Surinfett.*
Italian—*Sego di Surin.*

Surin fat is probably derived from the seeds of a species of *Palaquium.*
A specimen obtained by the author from the Imperial Institute was
described as " Minyak surin, from Perak, Straits Settlement." After
removing some impurities by filtering, the following characteristics
were ascertained in a sample containing 43·2 per cent of free fatty
acids.

Fat—

Specific gravity at 60° C. (water at 60° C. =1) .	0·9021
Solidifying point, commences to solidify at ° C. .	48·9
„ „ solid at ° C. .	43·90
Melting point (capillary tube), ° C. .	56·1
Saponification value .	179·5
Unsaponifiable matter, per cent .	4·54
Iodine value . .	42·31
Reichert-Wollny value .	0·55

Fatty Acids—

Solidifying point, ° C. .	59·1
Mean molecular weight .	284·9
Stearic acid (of melting point 67·8° C.), per cent	58·2

Evidently the fatty acids consist of a mixture of stearic acid and
oleic acid only. The extremely high proportion of stearic acid would
seem to render this fat a very useful raw material for the candle
industry, although the considerable amount of unsaponifiable matter
might militate against its use. (Possibly the high proportion of
unsaponifiable matter is due to careless preparation of the fat.)

Although a number of species (eighteen) of the genus *Palaquium*
(family of *Sapotaceæ*), all of which yield gutta-percha, have been
described, the fats obtainable from them are hardly known. The
seeds of *Palaquium pisang*, Burck (Sumatra), are stated to yield 45
per cent of a bitter, yellowish fat, known in commerce under the name
" Balam tallow."

From the seeds of *Palaquium oleosum*, Blanco (Sumatra), a white
sweetish fat (" Suntei tallow ") is expressed. *Palaquium oblongifolium*,
Burck (Borneo), is said to yield a hard white fat (" Njatuo tallow ")
consisting chiefly of " stearine " (whatever this may mean). It is
used in West Borneo as an edible fat. *De Jongh and Tromp de Haas* [2]
described the fat from *Palaquium oblongifolium*, Burck (which yields
the best kind of gutta-percha), and gave the following figures :—

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[1] Lewkowitsch, *Analyst*, 1906, 2.
[2] *Chem. Revue*, 1904, 285.

Yield of fat from seeds	.	.	.	32·5 per cent
Melting point of fat	. .	.	.	40° C.
Saponification value	.	.	.	201·5
Iodine value	.	.	.	34·3

The specimen examined by them was comparatively fresh, as the percentage of free fatty acid was only 2·1. It is stated to consist of 57·5 per cent of stearin, 36 per cent of olein, and 6·5 per cent of palmitin.

The oil from a species of *Palaquium* examined by *Boutoux* gave the following characteristics :—

Oil—

Solidifying point, ° C.	.	.	.	30
Melting point, ° C. .		.	.	38·5
Saponification value	.	.	.	177·7·182·3
Iodine value	.	.	.	48·2·57·2

Fatty Acids—

Titer test, ° C.	.	.	.	54·8
Melting point, ° C. .	.	.	.	57
Neutralisation value	.	.	.	181·1·182·8

Obviously " Surin fat " does not differ much from the fat of *Palaquium oblongifolium*.

MKÁNYI FAT

French—*Suif de Mkany.*   German—*Mkanyifett.*
Italian—*Sego di Mkany.*

This fat forms about 67 per cent of the seeds of *Stearodendron Stuhlmannii*, Engl. (*Allanblackia Stuhlmannii*, Engl.), an East African *Guttifera* (called Mkányi by the natives of Uluguru). The fruits, 22 cm. long and 15 cm. broad, enclose about 30 seeds, resembling chestnuts in form.

The fat, as prepared by the natives, is of yellowish-white colour ; it is sold at Bogamoyo in lumps having the shape of ostrich eggs and weighing from 700 to 800 grms. The acid values of various specimens of the native product were 23·33 (*Heise*) ; 11·6-20·7 (*Henriques*). According to *Heise*,[1] who first examined this fat, Mkányi fat consists chiefly of the mixed glyceride, oleodistearin (Chap. I.). No palmitic acid was found in the fat.

[1] Heise, *Arb. a. d. kaiserl. Gesundheitsamte*, 1896, 540.

Physical and Chemical Characteristics of Mkányi Fat

Specific Gravity		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.	
At °C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
15	0·9298	38 at 39 crystals appear, remains liquid to 29·5, rising on solidifying to 36°.	Heise Henriques	40-41 completely melted at 42.	Heise Henriques	190·5 186·6, 191·7	Heise Henriques	41·9	Heise	1·21	Heise
40	0·8926										
98 (water 15°=1)	0·85606										
100	0·8606										

Observers (Specific Gravity): Henriques and Kunne; Heise; ,, ; Henriques

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point		Melting Point.		Iodine Value.	
Per cent	Observer	°C.	Observer.	°C.	Observer.	Per cent	Observer.
95·65	Heise	57·5	Heise	59	Heise	42·1	Henriques
		61·4-61·6 (Titer test)	Henriques	61·5	Henriques		

French—*Suif de Rambutan.*   German—*Rambutantalg.*
Italian—*Sego di Rambutan.*

Rambutan tallow is obtained from the seeds of *Nephelium lappa-ceum*, L., indigenous to China and the Sunda islands. The seeds contain 40-48 por cent of fat.

Physical and Chemical Characteristics of Rambutan Tallow

Specific Gravity	Solidifying Point	Melting Point	Saponific Value	Iodine Value.
	°C.	°C.		
0·9236	38-39	42-46	193 8	39·4

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.	Melting Point	Neutralisation Value	Mean Molecular Weight.	Iodine Value
°C.	°C.			
57	58-61	186·4	300·9	41·0

The high mean molecular weight of the insoluble fatty acids indicates the presence of fatty acids higher than stearic acid; indeed, arachidic acid was isolated, as also a small quantity of stearic acid; palmitic acid is stated to be absent. The proportion of oleic acid in the insoluble fatty acids was found to be 45·5 per cent.

MALABAR TALLOW, PINEY TALLOW [2]

French—*Suif de Piney (Malabar).*   German—*Malabartalg, Vateriafett, Pineytalg, Pflanzentalg.*   Italian—*Sego di Piney.*

For tables of characteristics see p. 578.

This fat is obtained from the seeds of *Vateria indica*, L., a large evergreen tree indigenous to the East Indies, which yields the " piney resin " or white dammar of South India, or Indian copal (" vellai-Kungiliam "). The tree occurs especially in the Western Peninsula from Kanara to Travancore, and is found at an altitude of 4000 feet; it is known locally as " Dupada " and " Pinne." The fat is extracted by grinding the roasted seed and boiling the meal with water, when the melted fat rises to the top and is skimmed off.

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[1] Baczewski, *Journ. Soc. Chem. Ind.*, 1895, 1049 ; *Monatsh. f. Chem.*, 1895, 866.
[2] Wagner's *Jahresbericht*, 1884, 1186.

Physical and Chemical Characteristics of Malabar Tallow

Specific Gravity		Solidifying Point		Melting Point		Saponification Value		Iodine Value		Reichert-Meissl Value		Viscosity	
At °C.	Observer	°C.	Observer	°C.	Observer	Mgrms. KOH	Observer	Per cent.	Observer	c.c. $\frac{1}{10}$ norm. KOH	Observer	Seconds at 140° F.	Observer
9·4	0·9102 Dal Sie	30·5	Vierthaler and Bottura	36·5	Vierthaler and Bottura	191·9	Hohnel and Wolfbauer	37·82-39·63	Crossley and Le Sueur	0·22-0·44	Crossley and Le Sueur	101·5-104	Crossley and Le Sueur
15	0·915 Hohnel and Wolfbauer Crossley and Le Sueur			30	Dal Sie	188·7-189·3	Crossley and Le Sueur						
100 (water at 100=1)	0·8990-0·8907			42	Hohnel and Wolfbauer								
				37-37·5	Crossley and Le Sueur								

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point		Melting Point	
°C.	Observer	°C.	Observer
54·8	Hohnel and Wolfbauer	56·6	Hohnel and Wolfbauer

Malabar tallow is free from taste and odour. In the fresh state it has a greenish-yellow colour which on exposure to the air is rapidly bleached. Its consistence approaches that of mutton tallow. The commercial fat contains about 2 per cent of a pleasantly smelling volatile oil, which can be extracted with alcohol. Two samples of fat examined by *Crossley and Le Sueur* [1] had the acid values 5·18 and 15·34 respectively.

The specimen of Malabar tallow examined by *Hohnel and Wolfbauer* consisted of 19 per cent of free fatty acids and 81 per cent of glycerides. The solid fatty acids melted at 63·8° C.

In India Malabar tallow is used as an edible fat.

CACAO [2] BUTTER

French—*Beurre de cacao.* German—*Kakaobutter.*
Italian—*Burro di cacao.*

For table of characteristics see pp. 588, 589.

Cacao butter is expressed from the cacao beans, the seeds of the cacao tree, *Theobroma cacao*, L.[3]

This tree is indigenous to the West Indies. As its cultivation is remunerative, it has been introduced into various tropical countries, especially Central and South America. The cultivation of the tree on the West Coast of Africa has also been attended with success, and considerable quantities of cacao beans from Nigeria, etc., are shipped to Europe. The cacao pods are cut open by hand, and the beans, of which the pods contain from 25 to 40, are brought into fermenting sheds, where they undergo rotting, *i.e.* a kind of fermentation. The fermented beans are then dried either by exposure to the sun or with hot air. In the course of this fermentation the aromatic substances characteristic of cacao are formed. At present even vacuum plant is being introduced into the West African cacao plantations, so as to dry [4] the beans in as expeditious a manner as possible before shipping them to Europe. The experimental cultivation of the cacao tree in Dahomey gave very good results, but has not led to commercial success owing to the competition of the neighbouring colonies.

The following tables give some data as to the extent of the production of cacao and the imports into the most important countries [5] : —

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[1] *Journ. Soc. Chem. Ind.*, 1899, 991.

[2] I prefer the spelling "cacao" to "cocoa," in order to avoid the confounding of this fat with cocoa nut oil or kokum butter.

[3] For a useful summary of our knowledge regarding the botany, chemistry, and diseases of the cacao tree, cp. H. Wright, *Theobroma Cacao or Coco*, Colombo, 1907.

[4] A description of a drying house for cacao erected in Trinidad is given in the *Quart. Journ. Inst. Comm. Research in the Tropics* (Liverpool University), 1907, vol. ii. No. 5, 121 ; cp. also Leehmann, *Kakao und Schokolade*, Hannover, 1909.

[5] Cp. O. Rohdich, *Inaug. Dissert.*, Jena, 1908. It may be added that about one-fifth of the world's supply of cocoa comes at present from San Thomé and Principe.

Production of Cacao Beans

		1905.	1906.	1907.	1908.	1909.	1910.	1911.
		Kilograms.	Kilograms.	Kilograms.	Pounds.	Pounds.	Pounds.	Pounds.
Venezuela	Caracas	6,955,629	6,524,878	7,056,324	35,942,400	37,142,765	38,081,055	39,683,200
	Carupano	3,106,864	2,657,637	3,689,471				
Ecuador	Guayaqul	1,604,200	20,711,500	18,285,000	70,810,413	69,386,190	80,039,255	88,846,285
Brazil	Bahia	17,123,400	22,681,620	23,361,000	72,655,441	74,555,926	64,281,448	85,980,300
	Parakako		2,104,751	3,517,432				
British	Trinidad	22,520,700	13,262,050	18,869,940	47,112,965	51,566,224	57,829,184	53,351,825
West Indies	Grenada	5,796,575	4,940,030	3,433,830	11,373,271	11,996,267	12,889,059	13,227,700
	San Thomé	29,947,952	28,707,560	28,226,310	63,334,365	66,714,107	80,831,976	73,854,810
Dominican Republic		12,644,952	14,328,482	10,955,650	41,899,004	32,667,070	36,603,667	44,092,400
British West Africa		5,179,054	9,084,314	11,376,608	28,541,053	45,269,805	50,952,135	77,161,800
Other countries (estimated)		30,124,613	33,586,000	26,101,791	64,288,359	64,268,359	65,554,298	19,622,665

The world's production and consumption of raw cocoa is given below :—

	World's Production.	World's Consumption
	Metric tons	Metric tons.
1905	144,442	143,566
1906	147,468	156,785
1907	150,444	156,557
1908	193,753	165,141
1909	206,337	194,838
1910	219,562	201,166
1911	244,545	229,988
1912	247,000	245,000

Import of Cacao Beans during January to August

Into	1905.	1906.	1907.	1908.	1909.	1910.
	Kilograms.	Kilograms.	Kilograms.	Pounds.	Pounds.	Pounds.
United States of America	43,174,175	.	56,024,400	97,419,700	121,369,552	115,843,881
Germany	49,187,870	51,971,560	53,868,910	.	89,782,840	96,874,011
France	36,891,950	37,917,440	41,845,600	120,828,660	116,519,620	134,516,172
United Kingdom	22,986,462	25,121,648	23,473,322	66,833,413	77,032,263	70,650,300
Belgium	1,982,782	2,479,026	2,085,997	15,035,389	19,058,673	21,784,384
Holland	26,248,400	31,707,300	32,844,500	55,643,845	68,753,360	..
Spain .	8,484,200	8,615,800	9,200,000	13,916,872	13,184,409	12,163,359

The beans are chiefly worked up for the preparation of cacao; hence cacao butter is to some extent a by-product of this industry.

The cacao beans are roasted over coke fires (similarly as coffee is roasted), after being cleaned in a suitable manner (in a machine or by hand-picking).

In order to illustrate the changes which take place in roasting the cacao bean, the following table due to *Booth, Cribb and Richards* [1] may be given here : —

Constituents.	Grenada Bean (with Shell).		Trinidad Bean (without Shell).	
	Raw.	Roast.	Raw.	Roast.
Moisture	6·32	3 40	6·67	4·45
Fat	46·50	46 96	54 60	55 70
Nitrogen	1·96	1 86	2 28	2 32
Fibre .	3 60	3 90	2 45	2 48
Total ash	2 86	3 12	2·87	2 73
Siliceous matter	0 10	0·12	0 03	0·08
Soluble ash .	1 26	1 44	0 94	0 95
Alkali, as K_2O	0 68	0 75	0·42	0·43
Cold-water extract	13·50	12 90	12·73	12 00

[1] *Analyst*, 1909, 137.

The composition of the *cacao butter* is not affected by the roasting. This has been specially shown by *Heiduschka and Herb* [1] when examining cacao fruits which had been preserved in brine. The roasted beans are cooled as rapidly as possible, so as to prevent spontaneous heating. Next the husks are separated by passing the beans through rollers, when the thin shell is cracked without the kernel proper being broken ; the lighter shell is then removed by an air blast ("winnowing"). The shells are mostly sold under the name of "shell cacao" as a cattle food. Since the shells contain from 3 to 6 per cent of fat, this is recovered in some works and sold as "cacao shell butter." The examination of some commercial cocoa-shell butters is given below.

Welmans [2] pointed out that the iodine value and acid value of cacao-shell butter are higher than those of the corresponding cacao butters.

The author recently examined two samples of cacao butter with the following results :—

Free fatty acids, per cent	2·0	4·2
Saponification value	191·9	188·4
Iodine value	40 86	40 38
Unsaponifiable matter, per cent	1·75	3 08

These are obviously prepared from cacao shell.

A sample examined by the author of cacao butter prepared from shell of known origin had the following characteristics :—

Saponification value	188 1
Iodine value	41·7
Unsaponifiable matter, per cent	2 6
Butyro-refractometer at 40° C.	48
Titer test of fatty acids, ° C.	48 4

Procknow [3] found the iodine values enumerated in the third column of the following table :—

Origin.	Fat in the Roasted Shells.	Iodine Value of Fat.
	Per cent.	Per cent.
Ariba	4·39	44·1
Bahia	4·44	46 2
Caracas	4·33	44 9
Guajaquil	3·33	44·0
Thomé	5·64	43·2
Trinidad	2·28	45·15

The kernels remaining after winnowing are ground under millstones and reduced to a paste.[4] The bulk of the fat is then removed by hot expression in hydraulic presses. Before the ground material is put

[1] *Pharm. Centralh.*, 1908, 375.
[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905 (9), 263.
[3] *Inaug. Dissert.*, Wurzburg, 1909.
[4] Cp. F. E. F. Neumann, French patent 330,616 ; L. Hildebrand, German patent 239,974 ; P. Franke and Co., and Most, English patent 5232, 1913.

into the presses alkali carbonates are added ; [1] some manufacturers also
add the carbonates before roasting. As the alkali will combine with
any free fatty acids, the manufactured product is practically devoid
of free fatty acids, and the soaps are likely to pass into the expressed
fat. Hence in the examination of cacao butter the presence of ammonia
may be expected, and the ash should be determined. *A. Behre* [2] gives
the following analysis of the ash of cacao :—

CaO	. 10·12	P_2O_5 .	17·81
MgO	. 10·12	SiO_2	3·67
$Fe_2O_3 + Al_2O_3$	4·07	SO_3	17·63
K_2O	36·23	CO_2	5·64
Na_2O	. 0·60	Cl	. 0·83
			106·72

Cocoa prepared from unripe beans has an exceedingly bitter taste.
Kässmodel [3] patents a method for separating the unripe beans. *Strube* [4]
has shown that the different methods of treating the cacao mass have
no influence on the properties of cacao butter.

It is likely that in Germany cacao powders containing less than 20
per cent of cacao butter will have to be declared specially as such.
In order to press the cacao bean meal so that the cakes contain less
than 20 per cent of cacao butter, it is necessary to subject the mass,
after the bulk of the fat has been expressed at a low pressure (say 50
atmospheres) for some prolonged time to a pressure of at least 200
atmospheres in the hot press. According to experiments by *Böhme* [5]
it was not possible to obtain a mass containing less than 20 per cent
of fat, if the pressure was maintained for a period of 40 minutes only,
the lowest percentage having been 20·61 per cent (calculated to dry
substance, 21 per cent) In order to obtain a mass containing less
than 20 per cent of fat it is necessary to press at 200 atmospheres in
the hot for about $1\text{-}1\frac{1}{2}$ hours, or to use a higher pressure.

The percentage of fat in the beans has nothing to do with the
ultimate content of fat in the expressed mass, for if the beans were
very poor in fat, so much less butter would run off in the preliminary
expression. In order to prepare cacao mass, which only retains 15-16
per cent of fat (calculated to dry substance), it is necessary to allow
a pressure of at least 350 atmospheres or 400 atmospheres for some
prolonged time.[6]

A combined hydraulic- and filter-press for the separation of cacao
butter is patented by *M. A. Smith*.[7]

The proportion of fat in the beans varies from 50 to 56·5 per cent.
In determining the fat in the beans great care must be exercised in
disintegrating them. It will be found best to extract preliminarily

[1] Usually a 10 per cent solution of potassium carbonate is employed. As a rule,
one litre of this solution is added to 100 kg. of cacao mass. Some manufacturers use a
litre of ammonia for the same quantity of cacao mass.

[2] *Zeits. f. Unters. d. Nahrgs. u. Genussm.*, 1908, XVI. 421.

[3] German patent 217,288.

[4] *Zeitschr. f. öffentl. Chem.*, 1908, 67.   [5] *Chem. Zeit.*, 1908, 98, 110.

[6] Cp. P. Welmans, *Pharm. Zeit.*, 1907 (52), 891 ; L. Weil, *ibid.* p. 913 ; F. Müller.,
ibid., 1908 (53), 57.   [7] French patent 388,077.

the bulk of the fat from the finely-divided mass, then to dry, grind up with sand, and exhaust completely.

According to *Davies and M'Lellan*,[1] the roasted cacao beans are best extracted with petroleum ether of boiling point 40° C. to 50° C. Common ether extracts 0·2-0·5 per cent more than petroleum ether,[2] theobromine and some colouring matter being dissolved by the common ether. The following percentages of fat were ascertained in roasted nibs by *Davies and M'Lellan* :—

Country.	Fat. Per cent.
Ecuador, Arriba	54·66
„ other varieties	52·87
Venezuela, East of Caracas	51·33
„ West of Caracas	53·05
Dutch Guiana, Surinam	56·37
Brazil, Para	54·98
„ Bahia	54·33
Africa, West Coast	54·18
West Indies, Trinidad	54·57
„ Grenada	55·30
„ Dominica	56·03
„ Santo Domingo, " Samana "	55·38
Jamaica	56·57
Ceylon	53·36

These results may be supplemented by some later analyses published by *Genin*,[3] who used petroleum ether for extraction.

Origin.	Water	Fat.	Fat calculated to Dry Substance.
	Per cent.	Per cent.	Per cent.
Bahia	2·00	54·60	55·71
Para I.	2·70	55·50	57·04
Para II.	1·80	56·90	57·94
Caracas I.	2·52	52·80	54·16
Caracas II.	2·10	54·70	55·87
Carupano I.	2·50	53·60	54·97
Carupano II.	2·15	54·13	55·32
Trinidad I.	2·84	53·70	55·27
Trinidad II.	2·94	51·70	53·26
Sanchez I.	3·40	53·27	55·14
Sanchez II	2·12	52·50	53·63
Martinique I	2·10	54·70	56·04
Martinique II.	2·74	53·20	54·69
Guadeloupe	2·24	54·40	55·64
Santa Lucia I.	2·08	56·10	57·29
Santa Lucia II.	2·53	54·80	56·22
Santa Lucia III.	2·81	53·40	54·94
Grenada I.	3·10	54·20	55·93
Grenada II.	3·05	54·00	55·69
Accra (Africa) I	2·54	54·90	56·33
Accra (Africa) II	1·96	53·80	54·87
Congo	2·51	54·90	56·31

[1] *Journ. Soc. Chem. Ind.*, 1904, 480.
[2] Nevertheless the German official method directs the use of ether; see Procknow, *Arch. Pharm.*, 1910 (248), 81
[3] *Rev. génér. chim. pure et appliq.*, 1907 (x.), 303.

As the shells contain a notable amount of theobromine—as a rule 0·75 per cent—the recovery of the latter has become a remunerative operation. The removal of the fat being necessary before the theobromine can be recovered, the husks are extracted with petroleum ether and other solvents from which the dissolved fat is recovered. This extracted cacao butter is, of course, unfit for consumption ; nevertheless attempts are being made to sell such cacao butter to chocolate manufacturers. The shells freed from fat and theobromine are also offered as cattle food, and on account of their high nutritive value they find an outlet on the Continent, especially where extracted palm kernel cakes are not objected to (cp. p. 618). The proper use of the extracted cacao shells, however, appears to be as fertiliser, for which it is especially suitable on account of its comparative high proportion of nitrogen and potassium.

The cacao beans destined for the manufacture of best chocolate are roasted and freed from shells, as described above, but are not expressed, so that the full amount of fat remains in the ground mass. For the detection of cacao shell in the ground mass by means of its specific gravity the original papers must be consulted.[1] This is then mixed with sugar and arrowroot, and in the case of milk chocolate with cow's milk.[2] Some chocolate manufacturers, however, express part of the cacao butter and sell it as such, substituting the amount expressed from the cacao mass by " chocolate fats " (see Vol. III. Chap. XV.).

Cacao butter has a yellowish-white colour, turning white on keeping. It possesses an agreeable taste and pleasant odour like chocolate. At the ordinary temperature it is somewhat brittle.

Amongst the solid cacao butter fatty acids, stearic, palmitic, and arachidic acids have been detected, but the occurrence of lauric acid is doubtful (cp. Traub[3]). Heuduschka and Herb[4] could not detect caprylic acid. Theobromic acid, $C_{64}H_{128}O_2$, stated by Kingzett[5] to be present in the fat, is, according to Graf,[6] most likely arachidic acid. Stearic acid, first found in cacao butter by Stenhouse,[7] occurs to an extent of 39 (Lewkowitsch[8]), to 40 per cent (Hehner and Mitchell[9]). Farnsteiner obtained by the barium-salt-benzene method 59·7 per cent of solid acids, 31·2 per cent of oleic acid, and 6·3 per cent of other liquid acids. Linolic acid has been shown to occur in cacao butter by Benedikt and Hazura.[10] The statement that cacao butter contains formic, acetic, and butyric acids (which was supported by a high Reichert value recorded in the older literature) has been shown by the author to be erroneous.

Cacao butter appears to contain considerable amounts of mixed

[1] Dubois and Lott, Journ. Ind. and Eng. Chem., 1911, 251 ; Ullrich, Arch. d. Pharm., 1911, 524.

[2] Achor, French patent 419,832.   [3] Wagner's Jahresbericht, 1883, 1159.
[4] Chem. Zentralbl., 1908, ii. 90.
[5] Journ. Chem. Soc., 1878, 38.   [6] Arch. d. Pharm., 1888, 830.
[7] Liebig's Annal., 1840 (36), 56.
[8] Unpublished observations.   [9] Analyst, 1896, 328.
[10] Monatsh. f. Chem., 1889, 353.

glycerides. *Fritzweiler*[1] isolated from cacao butter about 6 per cent of oleodistearin. *Klimont* stated that he had isolated from cacao butter oleopalmitostearin and oleodipalmitin, but this appeared open to doubt, as his "oleopalmitostearin" had the low melting point of 31·33° C. (against *Hansen's* 42° C.). The renewed examination of cacao butter by *Klimont*[2] himself led him to withdraw his statement with regard to oleopalmitostearin, and he now states that cacao butter contains oleodistearin (found before him by *Fritzweiler*), as also oleo-dipalmitin (see Vol. 1. Chap. 1.). On allowing large quantities of "Samana" butter to cool slowly *Strube*[3] obtained a liquid portion, which differs from ordinary cacao butter in that it does not solidify readily. This liquid butter has the following characteristics :—Specific gravity at 17·5° C., 0·906 ; melting point about 12° C. ; iodine value, 53·6-58·8 ; butyro-refractometer at 40° C., 50·45 "degrees."

Strube[4] observed also a separation of a liquid portion from "Thomé" cacao butter. In this case, however, the liquid portion differed very little from normal cacao butter in its characteristics, only the acid value was found somewhat higher, viz. 7·7.

Röhrig[5] found for the liquid portion an iodine value of 56·6 and the butyro-refractometer reading of 51·8.

Matthes and Rohdich[6] examined the unsaponifiable matter of cacao butter. They obtained from 13 kilograms. of fat 28 grms. of crude unsaponifiable matter, which yielded 22 grms. of "crude phytosterol," and 6 grms. of an ethereal, oxygen-containing oil, smelling of hyacinths. The refractive index of this oil at 40° C. was 1·492, the iodine value 68·58, and the optical rotation + 0·37° in 10 per cent benzene solution (the length of the tube is not stated).

The crude phytosterol consisted of a hydrocarbon of the composition $C_{30}H_{48}$ (most likely identical with amyrilene), stigmasterol (identified by the tetrabromo-derivative of its acetate), and (phytosterol or) sitosterol (identified by the melting points of its acetate, viz. 130° C., and of the dibromo-derivative of its acetate, viz. 135° C.). In a later communication[7] *Matthes and Rohdich* state that the two alcohols obtained from the tetrabromo- and the dibromo- derivatives melted respectively at 162-163° C. and at 139° C. ¬

In an investigation of the aromatic principle of the cacao bean *Bainbridge and Davies*[8] obtained 24 c.c. of an ethereal oil from 2000 kgs. of cacao nibs by distillation in a current of steam. In this they detected D-linalool.

L. Reutter[9] extracted the beans previously freed from volatile oils by steaming at 110° C. with hot dilute methyl-alcohol, the highly coloured alcoholic extract deposits microscopic crystals of cacaorine to which he ascribes the formula $C_{16}H_{21}O_6N_8$, melting point 184-185° C.

[1] *Arbeit. a. d. kaiserl Gesundheitsamte*, 1902, 371.

[2] *Monatsh. f. Chem.*, 1905, 563.

[3] *Zeitschr. f. offentl Chem.*, 1905, 215.   [4] *Ibid.*, 1908, 67.

[5] *Pharm. Zentralhalle*, 1910, 2.

[6] *Berichte*, 1908, 19.   [7] *Ibid.*, 1908, 1592.

[8] *Proc. Chem. Soc.*, 1912, 253.

[9] *Compt. rend.*, 1913, 1842.

In the pharmaceutical literature the statement was frequently made, and is still being copied into text-books, that cacao butter does not turn rancid. *Dieterich* contradicted this statement some years ago; the author then showed by an extended series of observations [1] that cacao butter does turn rancid like any other fat under conditions favouring hydrolysis and subsequent rancidity. The author proved this in a somewhat exaggerated manner by exposing fresh cacao butters to the atmosphere in sunlight, when rancidity set in within a few (three to four) days. But it is a matter of common experience that cacao butter exposed to light and air at the ordinary temperature will become rancid in the course of a month or two. It must be left undecided whether the older erroneous statements, based on somewhat limited experience, are due to the fact that cacao butter, owing to its high price, is kept in a more careful manner than ordinary fats, or whether the keeping properties are due to the aromatic substance in cacao butter, which retards the setting in of hydrolysis (much as lard is preserved by " benzoating," *i.e.* by suspending powdered benzoin in the melted fat and allowing it to remain therein for some time).

The statement that rancid cacao butter is obtained from mouldy beans is erroneous. Most shipments of cacao beans become mouldy in transit, but since the beans, in the first stage of manufacture, are roasted at a temperature from 130° to 140° C., the mould is destroyed, so that cacao butter prepared from these beans need not of necessity be rancid.

The acid value of commercial samples of cacao butter was found by *Dieterich* to be from 1 to 2·3. *Lewkowitsch* found in a large number of genuine fresh cacao butters acid values varying from 1·1 to 1·95. A sample that had been kept ten years in a sealed bottle had the acid value 1·6.

On account of its high price cacao butter is frequently adulterated and also wholly substituted by chocolate fats (see Chap. XV.). The latter consist chiefly of the " stearine " of cocoa nut and palm nut oils. They are readily differentiated from cacao butter by their *Reichert-Meissl* values, and especially by their low iodine values.

[1] Lewkowitsch. *Journ. Soc. Chem. Ind.*, 1899, 557

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Solidifying Point		Melting Point		Neutralisation Value		Iodine Value		Refractive Index		
Per cent.	Observer	°C.	Observer	°C	Observer	Mgrms. KOH.	Observer	Per cent.	Observer	At °C.		Observer
94·59	Bense-mann	51	Hübl	52	Hübl	190	Thorner	39·1	De Negri and Fabris	40	1·4475	W. B. Smith
				48-49	Bense-mann			32·6	Thorner	60	1·422	Thorner
				51-52								
		47·45	De Negri and Fabris	49-50	"							
				52-53								
		46·47	Thorner	48·50	De Negri and Fabris							
				49·50	Thorner							
		Titer Test.										
		48·3	Lewko-witsch									
		49·2	"									
		49·6	"									

Physical and Chemical Characteristics of Cacao Butter

Specific Gravity.1		Solidifying Point		Melting Point		Saponification Value		Iodine Value		Reichert-Meissl Value		Refractive Index		
At °C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH	Observer	Per cent.	Observer.	c.c. N/10 norm KOH	Observer.	At °C.		Observer.
15	Dieterich	25-26	Herbst	32-34	Hager	192-202	Filsinger	34	Huhl	0.23	Lewko-witsch	60	1.4496	Thorner
20	Rakusin	27.3	Rudorff	32.1 33.4	Filsinger	193.55	De Negri and Fabris	34.35.5	Filsinger	0.34	,,	40	1.4565 to 1.4575.2	Strohl
50	Allen	23-21.5	De Negri and Fabris	30-32	Dieterich	198-200	Thorner	35.62	De Negri and Fabris	0.3-5	,,			
(water 15.5=1)			Thorner	30-34		161.8	Lewko-witsch	32.8-41.72	Strohl	0.837	,,		Butyro-refractometer	
98	,,	23		33.5	Rudorff	191.5		34 3-37.6	Lewko-witsch			At 46 C. degrees		Observer.
0.8577				28-30	De Negri and Fabris							46-47.8		Strohl
(water 15.5=1)				32-33	Thorner							40-40.5		Mansfeld
				28-33	Lewko-witsch									

1 According to White (*Pharm. Journ.* 1898, 69) the specific gravity of cacao butter, when freshly melted rises gradually from 0.950 until it reaches its highest value 0.995 after a few days   4 Prepared in the laboratory, from mfrs.
2 Forty commercial samples.   3 Genuine cacao butter, kept ten years in a sealed bottle   7 Genuine Dutch cacao butter fresh.
5 Genuine English cacao butters, fresh   6 From nearly 100 samples

Less decisive are the indications furnished by the melting point of the fat itself; in this connection it should be noted that the freshly melted cacao butter shows a considerably lower melting point than the normal one, and only regains its normal (higher) melting point when the sample has been kept for several days (in a desiccator). When determining the melting point it is best to proceed as described in Chapter V.[1]

For the detection of "chocolate fats"[2] (sold under various fancy names, see Chap. XV.), in genuine cacao butter, the determination of the saponification value and of the iodine value will as a rule suffice. These substitutes considerably raise the saponification value, whilst they lower the iodine value. The "titer" test of the fatty acids is also considerably depressed by them. The determination of stearic acid may be carried out as a confirmatory test. It is then hardly necessary to determine the *Reichert-Meissl* value. Therefore, the proposal made by *Wauters*[3] to ascertain the presence of cocoa nut oil in cacao butter in the same manner as is done in butter fat (see "Butter Fat") would appear to be an unnecessary process.

The presence of vegetable oils, such as *almond oil, arachis oil, sesamé oil, hazel nut oil*, would be readily recognised, in the first instance, by an increase in the iodine value, and by the lowering of the solidifying and melting points of the insoluble fatty acids.

Bees' wax and paraffin wax (stated to have been employed as adulterants) will hardly be added now, as they are too easily detected (by a low saponification value and a considerable amount of unsaponifiable matter). The presence of bees' wax would also be indicated by a high acid value of the sample. Cacao butters of comparatively high acid values owe their acidity (in the absence of adulterants) either to rancidity (ascertainable by the taste), or to admixture with fat which has been extracted from cacao bean shells. Very likely the cacao butters in which *Filsinger* found as much as 28 per cent of free fatty acids had such an origin.

The most difficult problem was, until recently, to detect adulteration with tallow. *Hager's* aniline test, recommended for that purpose, has been found useless by the author; its description is therefore omitted here.[4]

Bjorklund's ether test may be recommended as a preliminary test. It is carried out as follows[5]:—Place about 3 grms. of the sample in a test-tube, add twice the weight of ether, at the temperature of 18° C., close the test-tube with a cork, and effect solution, if possible, by shaking. The fat should dissolve to a clear solution. Then immerse the tube in water at 0° C., and note the number of minutes which the liquid requires to become milky, or to deposit white flocks, and observe the temperature at which the solution becomes again clear when re-

[1] Cp. also Welmans, "Ueber Oleum Cacao," *Pharm. Zeit.*, 1900, 99.

[2] Grimme, *Chem. Revue*, 1914, 47.

[3] *Bulletin de l'Association Belge des Chimistes*, 1901, vol. xv. No. 3, March.

[4] See 2nd edition of this work, p. 529.

[5] *Zeits. f. analyt. Chem.*, 3, 233.

moved from the water. The following table gives *Bjorklund's* observations made on pure cacao butter and on samples mixed with tallow :—

	Turbidity at 0° C after Minutes	Clear Solution at °C
Pure cacao butter .	10-15	19-20
Cacao butter + 5 per cent of beef tallow ,	8	22
Cacao butter + 10 per cent of beef tallow ,	7	25

The author [1] found, however, that cacao butters containing as much as 10 per cent of tallow will dissolve in two parts of ether at 18° C., although requiring a little longer time than genuine cacao butter does. The chief indication to be relied upon is not, therefore, the number of minutes required for crystallisation - as the time will vary for different samples—but the characteristic way in which genuine cacao butter crystallises as compared with adulterated samples. In the former case tufts of distinct crystals appear at the bottom and the sides of the containing vessel, whereas five or more per cent of tallow are recognised by flocks separating from the cooled solution.[2]

The modification of *Bjorklund's* test recommended by *Filsinger*, viz. to dissolve two grms. of the sample in 6 c.c. of a mixture of 4 parts of ether and 1 part of alcohol, is scarcely an improvement, and cannot therefore be recommended.

A reliable method to detect the presence of tallow is afforded by the isolation of cholesterol from the unsaponifiable matter by means of its dibromide, and further by the phytosteryl acetate test. The microscopic examination for the presence of cholesterol crystals will not furnish decisive information (*Lewkowitsch*).[3] Nor can a reliable deduction be drawn from the melting point of the isolated alcohol. *Procknow* [4] found the melting point of the alcohols isolated from genuine cacao butter 138·7° C. and 138·6° C. respectively, which after recrystallisation gave in the first fractions 148·2 and 148·4 respectively.

The statement by *Sachs* [5] that Borneo tallow is used as an adulterant of cacao butter requires confirmation.

Cacao butter is a by-product in the manufacture of cocoa, and is therefore obtainable in large quantities. It is used in the manufacture of chocolates,[6] in confectionery, in pharmacy (nitro-glycerine tablets), and in the preparation of perfumes.

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1899, 557.
[2] Cowie and Brander, *Chemist and Druggist*, 1909, 227.
[3] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1899, 557.
[4] *Inaug. Dissert.*, Würzburg, 1909.
[5] *Chem. Revue*, 1907, 279.
[6] The introduction of additional cacao butter (which is largely practised in the manufacture of "fondants") over and above the natural proportion in the beans permits the incorporation of a larger amount of starch than can be added to the genuine cacao mass in the manufacture of chocolate.

CHINESE VEGETABLE TALLOW

French—*Suif végétal de Chine.*   German—*Chinesischer Talg ;
Stillingiatalg ; Vegetabilischer Talg.*   Italian—*Sego di Stillingia.*

For tables of characteristics see pp. 594-596.

Vegetable tallow is the hard fat which coats the seeds of the Chinese
tallow tree, *Stillingia sebifera*, Willd. (*Stillingia sinensis, Croton sebi-
ferum, Sapium sebiferum,* Roxb., *Excœcaria sebifera,* F. Mull., *Carum-
bium sebiferum*).[1] The tree grows wild in China.[2] Since it has been
cultivated there it has been introduced into Indo-China and the north
of India, where it grows luxuriantly, as also in the United Provinces of
the Panjaub (Punjaub).[3] The tree has also been introduced into
South Carolina.   In China the stillingia tree is regularly exploited for
both its leaves and seeds ; the fat, however, represents a secondary
product only. In Tonkin the tree is only cultivated for the sake of
its leaves, a decoction of which furnishes a colouring matter used for
dyeing silk.

The tree commences to produce at the age of four to five years,
and when it has reached its full development it yields about 25-30
kilos. of seed a year. 100 kilos. of the fruit yield about 30 kilos. of
mou-iéou (*i e.* vegetable tallow + stillingia oil), or 15 kilos. of *pi-yu*
(*i.e.* vegetable tallow), and 15 kilos. of *tsé-tiéou* or *ting-yu* (*i.e* stillingia
oil).

The fruit contains three oval seeds surrounded by a thick tallow-
like mass. The seeds themselves contain a brownish-yellow oil, which
has been described already (p. 89) under the name of stillingia oil.
Tortelli and Ruggeri, who prepared the solid fat and the oil from the
seeds separately, obtained 22 per cent of vegetable tallow and 19·2
per cent of stillingia oil. According to *Lemarie* (Director of Agri-
culture, Annam), the seeds of *Sapium sebiferum,* known locally as
" *cây-sôi,*" yield 69 per cent of shells and 31 per cent of kernels. The
shells are coated with 29·5 per cent of a white, solid fat, and the kernels
contain 59·5 per cent of oil. *Schindler and Waschata* [4] found 36·4 per
cent of vegetable tallow on the entire seed.

According to the process of manufacture employed, three products
are obtained. One process has for its object the separate production
of vegetable tallow and of stillingia oil. The seeds are either placed
in perforated cylinders and steamed, so that the fat melts and runs
off, or they are passed between fluted rollers which scrape off the outer
fat-coating without breaking the seed proper, when the scraped-off
mass is pressed in the hot in primitive wedge-presses. This product

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[1] *Bull. Imp. Inst.,* 1903, 209 ; " Les Arbres à suif de l'Indo-Chine," *Bull. économ.,*
1902, Hanoi.
[2] It is known by the name Mu-tsé-shou.
[3] Cp. D. Hooper, *Agricult. Ledger,* 1904, No. 2.
[4] *Zeitschr. f. das landw. Versuchsst. in Österr.,* 1904, 643.

is sold under the Chinese name "*pi-iéou*," or "*pi-yu*," and is known to the European candle-makers as "prima" vegetable tallow. The seeds are then removed and crushed separately for the recovery of the stillingia oil, "*tsé-tiéou*" or "*ting-yu*" (see p. 89).

In the second process the seeds, together with their coating of fat, are crushed, and a mixture of vegetable tallow and stillingia oil is thus obtained. The product from the latter process is naturally much softer than the true vegetable tallow; it has a lower melting point, and also a much higher iodine value. This second quality is sold under the name "*mou-iéou*," known to the European candle-makers as "secunda" vegetable tallow, and represents a mixture of "*pi-yu*" and "*ting-yu*."

Samples of vegetable tallow which have been prepared in the laboratory by extracting the crushed fruit with solvents, contain therefore stillingia oil, and such numbers as were given by *De Negri and Fabris* for vegetable tallow extracted by them from the seeds by means of ether and carbon bisulphide do not hold good for true vegetable tallow. Hence numbers referring to a mixture of vegetable tallow and stillingia oil have been omitted from the tables. Nor have numbers observed for commercial fats, which undoubtedly represent a mixture of the two kinds of products, been recorded here.

Crushed vegetable tallow, if free from stillingia oil, leaves no grease-spot on paper. The samples examined in the author's laboratory had acid values varying from 7·07 to 7·51. *De Negri and Fabris* found 2·4; *De Negri and Sburlati*,[1] 2·2; *Klimont*, 14·2; *Zay and Musciacco*, 22·5.

According to *Maskelyne*, vegetable tallow consists of palmitin and olein. A confirmation of this statement may be found in the fact that *Hehner and Mitchell*[2] obtained no stearic acid crystals from a specimen absorbing 22·87 per cent of iodine. This is further confirmed by *Klimont*,[3] who found in a commercial sample (of the iodine value 27·6) palmitic and oleic acids only.

On repeatedly crystallising vegetable tallow from acetone (*Klimont*),[3] oleodipalmitin was obtained. In *Klimont's* opinion, vegetable tallow consists chiefly of oleodipalmitin, with smaller quantities of tripalmitin.

Zay and Musciacco state that the mean molecular weight of the insoluble fatty acids is 231·4, and that they isolated volatile fatty acids of the molecular weight 132·8. The low molecular weight of the insoluble fatty acids would point to the presence of lauric acid. The number 231·4 stands in need of confirmation. On a large scale the fat yields 8-9 per cent of glycerine.

[1] *Journ. Soc. Chem. Ind.*, 1897, 339.
[2] *Analyst*, 1896, 328.   [3] *Monatsh. f. Chem.*, 1903, 408.

[TABLE

Physical and Chemical Characteristics of Vegetable Tallow

Specific Gravity		Solidifying Point.		Melting Point.		Saponification Value.	
At °C	Observer.	°C.	Observer.	°C.	Observer.	Mgrms KOH.	Observer.
15	0.918 Thomson and Wood	26.7	Thomson and Wood	44.5	Thomson and Wood	200.3 [3]	Lewkowitsch
15	0.915 Lemarié[1]	24.2-26.2 [2][3]	Lewkowitsch	43-46 [3]	Lewkowitsch	179 [3]	De Negri and Fabris
50	0.915 Jules Jean[2]	34 [3]	De Negri and Fabris	44 [3]	De Negri and Fabris	203.6 [3]	Hobein
		35.3	Hobein	35	Lemarié[1]	203.3 [4]	
		32.4		43-45	Hobein	199-202.2 [5]	De Negri & Sburlati
100 (water 15=1)	0.8600 Zay and Musciacco	27.2-31.1 [5]	De Negri & Sburlati	39-42		203.5	Klimont
		37.7	Zay and Musciacco	36.5-44.1 [5]	De Negri & Sburlati	231	Zay and Musciacco
				53.2	Jules Jean		
				36.4	Klimont		
				52.5	Zay and Musciacco		
15.5	0.890 Seifert	28.3	Seifert	33	Seifert	205.7	Seifert

[1] *Mou-téou* oil. [2] *Kritsch, f. angew. Chem.*, 1898, 250. [3] Commercial sample. [4] Prepared from the seeds by steaming.
[5] Ten samples of commercial fat : the lower melting fats no doubt consisted of *mou-téou* oil.

Physical and Chemical Characteristics of Vegetable Tallow—continued

| Iodine Value | | Reichert-Meissl Value | | Refractive Index | | | |
| | | | | Oleo-refractometer | | Butyro-refractometer | |
Per cent	Observer	c.c. n/10 norm KOH	Observer	"Degrees"	Observer	At "C. "Degrees"	Observer
32·1-32·3 [1]	Lewkowitsch	0·69	Zay and Musciacco	−23	Jules Jean		
22·87	Hefner and Mitchell						
35·5 [1]	Hobein						
28·5 [2]	De Negri & Sburlati						
28·5-37·7 [3]	Jules Jean					50	38	Zay and Musciacco
38·3	Zay and Musciacco						
19·0	Klimont						
27·6							
36·3	Seifert						

[1] Commercial sample.   [2] Prepared from the seeds by steaming.
[3] Ten samples of commercial fat; the lower melting fats no doubt consisted of *mou-iêou* oil.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Solidifying Point		Melting Point		Neutralisation Value		Iodine Value	
Per cent	Observer	°C	Observer	°C	Observer	Mgrms. KOH	Observer	Per cent	Observer
93·45	Zay and Musciacco	Titer Test							
		52 1-53·5 [1]	Lewkowitsch	56·57	Mayer	182 1 [1]	De Negri and Fabris	34·2-34 3 [1]	Lewkowitsch
		42 [1]	De Negri and Fabris	47 [1]	De Negri and Fabris			17 [1]	De Negri and Fabris
		41 [1]	Hobein	51 [1]	Hobein	207 9 [1]	Hobein	54·1-54·8	Hobein
		40 [2]		49 [2]		206 4 [2]		38·1 [1]	,,
								29·2 [2]	
		45 2-47·9 [3]	De Negri and Sburlati, Jules Jean	53-56 9 [3]	De Negri and Sburlati, Jules Jean	202-208·5 [3]	De Negri and Sburlati	30·3-39 5 [3]	De Negri & Sburlati, Seifert
		56·4	Seifert	56·8				45·8	
								Liquid Fatty Acids	
95·7 [4]	Seifert	52·7	Seifert			240·1 (?)	Zay and Musciacco	97·04	Zay and Musciacco

[1] Various commercial samples.   [2] Prepared from the seeds by steaming.

[3] Ten samples of commercial fat; the lower melting fats no doubt consisted of *mou-tou* oil.

[4] Unsaponifiable matter 0 95 per cent.

The production of vegetable tallow in China is very large, and has been practised there for many centuries. The fat is used extensively for the manufacture of candles. Hankow is the central market whence the bulk of Chinese tallow is shipped. Before the material reaches Hankow it undergoes at Tchang-té-fou the first manipulation, consisting in the mixing of the *mou-iéou* with the *pi-yu*. Thus the intermediate quality is obtained, known as "secunda vegetable tallow," whilst the pure *pi-iéou* is termed "prima quality." At Hankow it undergoes the final purification, being remelted and freed from fraudulently added foreign substances. It is then cast into blocks, in which form the fat is received in Europe. The first considerable quantities came into the European market in 1894. The chief countries which import vegetable tallow are Italy, the United Kingdom, and France. Small quantities only are bought by the United States. Only the two qualities *mou-iéou* and *ting-yu* are exported.

In 1907 about 4000 tons had been imported by this country ; the order of consuming countries is now arranged in order of quantities : United Kingdom, 4000 tons ; France, 2500 tons ; Italy, 1700 tons.[1] In 1909 and 1910 the total exports from Hankow were 9029 and 9482 tons respectively, and in 1911 and 1912 the total exports were 4776 tons and 10,735 tons respectively.

KOKUM BUTTER, GOA BUTTER, MANGOSTEEN OIL

French—*Beurre de kokum.* German—*Kokumbutter.*
Italian—*Sego di kokum.*

For tables of characteristics see p. 599.

This fat is obtained in the East Indies from the seeds of the Guttifera, *Garcinia indica*, Choisy, *Garcinia purpurea*, Roxb. (*Mangostana indica*, L., *Brindonia indica*, Du Pet.). The seeds contain 20-25 per cent of fat.

The fat is prepared in India—especially on the West Coast, between Daman and Goa—in a primitive fashion, by drying the seeds in the sun and boiling them out with water. The fat is then skimmed off, filtered in a crude fashion, and cast into round cakes weighing about 100 grms. each, in which form it is sold in the Indian bazaars.

Kokum butter is a white or light grey fat, having a slight, not disagreeable odour, and a mild oily taste.

The acid constituents of kokum butter are oleic and stearic acids,

[1] *Journ. Soc. Chem. Ind.*, 1909, 209.

with small quantities of (probably) laurie acid. According to *Heise* [1] (confirmed by *D. Hooper* [2]), this fat (like Mkányi fat) consists chiefly of oleodistearin. The specimen examined by *Heise* contained 10·5 per cent of free fatty acids, and that tested by *Crossley and Le Sueur* [3] 7·1 per cent, calculated as oleic acid.

Kokum butter is chiefly used as an edible fat, and is stated to be employed for the adulteration of " Indian butter." It is also used in pharmacy for ointments, etc. The kokum butter which is unfit for edible purposes is worked up for soap.

Other species of *Garcinia* (cp. " *Gamboge* Butter," p. 551) yield similar fats, which have not been examined fully, such as—

(1) The fat from *Garcinia pictoria*, Roxb. This fat is chiefly obtained in the western district of Mysore, where it is used as an edible fat by the poorer classes. The bulk of the fat which has become rancid, being unfit for consumption, is used as a burning oil.

(2) The fat from *Garcinia tonkinensis*, Vesqu. (*Garcinia Balansœ*, Pierre; H. Baillon), the *Cây gioc* or *Cây doc* of the Annamites. *Garcinia Mangostana* L.[4] occurs widely in Cochin China, Annam, Réunion, French Guiana, where the fruits are used for edible purposes. The seeds are from 2 to 3 cm. long and 1·5 cm. wide. The weight of the seed is 2 to 3 grms., and it consists of 4·8 per cent shell and 95·2 per cent kernels. The kernels contain 63·4 per cent of oil ; the yield from the whole seed being 61·8. By extraction with ether a dark brown oil was obtained, which had the following characteristics (*Grimme* [5]) :—

Oil—

Specific gravity at 15° C .	0 9127
Solidifying point, ° C. .	3·2
Melting point, ° C. .	8 6
Saponification value	176·3
Iodine value	86·2
Acid value .	19·9
Refractive index at 40° C.	1·4682

Fatty Acids—

Insoluble acids + unsaponifiable, per cent	93·18
Unsaponifiable, per cent .	4·23
Solidifying point, ° C.	30·3
Melting point, ° C. .	32·5
Neutralisation value	161·8
Iodine value	89·1
Refractive index at 60° C.	1·4564
Mean molecular weight .	341·4

[1] *Arbeiten a. d. kaiserl. Gesundheitsamte*, 1896, 13, 302.
[2] *Journ. and Proceed. of the Asiatic Soc. of Bengal*, 1907, iii. 257-259.
[3] *Journ. Soc. Chem. Ind.*, 1898, 991.
[4] Heckel, *Les Matières grasses*, 1909, 1623, 1923.
[5] *Chem. Revue*, 1910, 264.

Physical and Chemical Characteristics of Kokum Butter

Specific Gravity			Solidifying Point		Melting Point		Saponification Value		Iodine Value		Reichert-Meissl Value		Refractive Index		
At °C.		Observer	°C.	Observer	°C.	Observer	Mgrms. KOH.	Observer	Per cent.	Observer	c.c. $\frac{1}{10}$ norm. KOH.	Observer	At °C.		Observer
40 (water 15°=1)	0·8952	Heise	33·3	Redwood	36·7	Redwood	191·3	Heise	33·1	Heise	1·54	Heise	25	1·4628 [2]	Heise
98 (water 15°=1)	0·8574	"	27·5	Fluckiger and Hanbury	42·5	Fluckiger and Hanbury	196·8	Crossley and Le Sueur	34·2	Crossley and Le Sueur	0·11	Crossley and Le Sueur	40	1·4565 [2]	Crossley and Le Sueur
100 (water 100°=1)	0·8889	Crossley and Le Sueur	37·6	Heise [1]	45	Heise [1]									
			37·9		41-42	Heise [1]									
					42	Crossley and Le Sueur									
					43	Hooper	191·5	Hooper	25	Hooper	0·98	Hooper			

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Solidifying Point	Melting Point	Mean Molecular Weight	Observer
Per cent.	Observer	°C.	°C.		
95·59	Heise				
94·59	Crossley and Le Sueur	59·4	60·61	282	Heise
93·5	Hooper	...	61	...	Hooper

[1] The melting point varied according as to whether the melted fat was allowed to solidify rapidly at 0° C., or kept at the ordinary temperature; in the former case the melting point was 32°-33° C., in the latter it rose to 40° C. after 24 hours standing (cp. Chap. V.).

[2] Calculated from observations made with the butyro-refractometer.

It is stated to contain 4·6 per cent of an ethereal oil, and nearly 6 per cent of resinous substances [1] (these numbers require confirmation). *Bontoux* states that two different resins are contained in these fats, one consisting of hydrocarbons, and resembling caoutchouc, and the other a saponifiable resin. The fat is used as a burning and a lubricating oil. If more care were taken in the preparation of this oil the amount of unsaponifiable matter might perhaps be reduced, and it would then be suitable for soap-making.

(3) *Garcinia echinocarpa*, locally known in India as "madol oil." [2] The seeds yield a thick oil, which is used as a burning oil, and also for medicinal purposes (as a vermifuge).

BORNEO TALLOW [3] TANGKAWANG FAT

French—*Suif végétale de Bornéo*   German—*Borneotalg. Tenkawangfett.*
Italian—*Sego di Borneo.*

Borneo tallow is obtained from the kernels of a large variety of plants belonging to the family of *Dipterocarpus*, as *Shorea stenoptera*, Burck., *Shorea aptera*, Burck., *Hopea aspera*, de Vriese, *Pentacme siamensis*, Kurz, *Shorea compressa*, *S. falcifera*, *S. gysbertiana*, *S. martiniana*, etc., indigenous to the Sunda Islands and Indo-China. [4] The native name of Borneo tallow is Minjak Tangkawang (Tangkawang Fat). The "minjak tangkawang" represents a mixture of at least six fats, obtained from six varieties of trees, known to the natives as *Tangkawang tangkal*, *T. rambei*, *T. lagar* (these trees have a diameter of more than 3 ft.), *T. goentjang* (growing in swampy regions and reaching a height of 22 ft., whilst the diameter of the trunk rarely exceeds 6 inches), *T. madjan*, *T. terindak*. The last two trees bear smaller fruits, which yield a fat containing about 3 per cent of unsaponifiable matter, which is apparently a natural resin, inasmuch as it imparts to the fat a viscous character. The first four trees grow wild on the west coast of Borneo, excepting on the strips of land bordering the Kapoea river. The "tangkawang trees" are also cultivated by the natives (chiefly in the districts of Sanggan and Sekadan). The trees flower in September and October, and the fruits ripen in February and March. [5]

The fat is prepared by the Annamites, according to *Lemarié*, in the following manner :—The hard fruits are left for some time in a damp place until the shells break and the seeds begin to germinate. They are then dried in the sun, and the kernels are separated from

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[1] Heim, *Moniteur officiel du Comm.*, 1901, August; *Bull. économ. de l'Indo-Chine*, Nouvelle série, No. 51.
[2] *Bull. Imp. Inst.*, 1901, June.
[3] Geitel, *Journ. Soc. Chem. Ind.*, 1888, 391.
[4] Pierre, *Flore forestière de la Cochinchine*, 1902.
[5] O. Sachs, *Chem. Revue*, 1907, 278.

the pericarp and placed in baskets of bamboo canes, which are suspended over pots of boiling water. When the kernels have become soft and pasty, they are placed in bags and pressed. The fat thus obtained is moulded in the internodes of bamboo stems; hence the commercial samples have a cylindrical shape

In Borneo the fat is obtained either by a "wet process" or by a "dry process."[1] The wet process consists in placing the fruits in baskets, which are then completely immersed in water, care being taken that the fruits cannot float to the surface, this being done to prevent germination. The immersion in water appears to be a process of preservation, the natives believing that in consequence of this process the fruits are not so easily attacked by the "boebuk" worm. After thirty to forty days the fruits are taken out of the water and the shells are removed. The kernels, which generally split up into four parts, are spread on boards and exposed to the sun to dry. In order to prevent absorption of moisture the fruits are either covered during the night or taken into tents. The dry kernels are termed "paddi-tangkawang."

The "paddi" obtained by a dry process, such as described, p. 600 (a process which is also in vogue in some districts of Borneo, e.g. Landak), is stated by the natives to furnish an inferior kind of product The following are the essential features of a third process (practised in Sanggan):- Immediately after collecting the fruit the kernels are cut into discs, dried by exposure to the sun, and pressed as described above. This process yields the so-called "tangkawang soutae." This latter quality is considered the best, and is used exclusively for edible purposes by the natives. It is impossible to give the percentage yield of fat from the fruits, it can only be stated that those from *Shorea stenoptera* yield about 50 per cent of fat.

In view of the great commercial importance Borneo tallow may acquire, further investigation is desirable. In commerce varieties of Borneo tallow are known under the names " Pontianak," " Sarawak," and "Siak" tallow. The " Pontianak " and " Sarawak " are obtained from the first four kinds of tangkawang mentioned above, and are notable for their hardness. Of the two kinds, " Pontianak " is the more valued. The " Siak " tallow is much softer and hence the less valued.

It should be pointed out that considerable confusion obtains in commerce with regard to the correct names of the " Pontianak," " Sarawak," and " Siak " fruits, which are imported and sold as " Illipé nuts " from Sarawak and Pontianak (" grosses graines de Pontianak et Sarawak ") and from Siak (" petites graines de Siak "). The former are the fruits of *Shorea stenoptera* and the latter the fruits from a *Palaquium* species (*Dichopsis*).

The characteristics of the fat from " Grosses graines de Pontiac " (undoubtedly a variety of *Shorea*, probably *Shorea stenoptera*) are given by *Bontoux* as follows :--

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[1] O. Sachs, *Chem. Revue*, 1907, 278.

Solidifying point, ° C.	.	.	.	29
Melting point, ° C.	.	.	.	36·5
Saponification value .	.	.	.	193·7
Iodine value .	.	.		28 8-31·2
Unsaponifiable matter	.			0 8
Titer test of fatty acids, ° C				52
Melting point .	.	.	.	54

These seeds known as " Variété rouge " contain 48-50 per cent of fat. For the " Variété noire," which contains 68-69 per cent of fat, *Bontoux* found the saponification value 201·7 and the iodine value 34·1-37·4.

In the following table I give some characteristics of the fat from *Shorea aptera*, Teglam fat, and of samples of unknown origin : –

Physical and Chemical Characteristics of Borneo Tallow (Tangkawang Fat)

Fat from	Specific Gravity at 100°C.	Melting Point. °C.	Solidifying Point. °C.	Saponification Value Mgrms. KOH.	Iodine Value. Per cent.	Butyro-Refractometer. °C.	Butyro-Refractometer. "Degrees."	Observer.
Shorea aptera	...	31	...	191·2	15 [1]	...	...	Heim
Teglam fat	...	...		192 2	16 [2]	...	...	"
"	0 856 (water at 15·5=1)	28·31	...	192 1	31 5	40	45·2	Brooks [4]
Commercial samples	...	35 36: 42	...		31 [3]	...		Geitel
"	...	34 5·34 7	...	194 6	30 1	...		Klimont [5]
"		42·45		193 8	29 4			Farnsteiner [6]
"	0 892	37·5	22	192 + 196	30·31			Sachs

[1] Calculated from Heim's statement that the sample contains 16 7 per cent of oleic acid.

[2] Calculated from Heim's statement that the sample contains 18 per cent of oleic acid.

[3] Calculated from Geitel's statement that the sample contains 34 per cent of oleic acid.

[4] *Analyst* 1909, 206.

[5] *Monatsh f. Chem.* 1904, 929.

[6] *Zeits. f. Unters. d. Nahrg.- u Genussm.,* 1906 (xi), 198. Butyro-refractometer at 40° C. 45 degrees. The phytosterol of the fat gives an acetate melting after the sixth crystallisation at 126° C

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Fat from	Insoluble Acids + Unsaponifiable. Per cent	Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight	Iodine Value Per cent	Observer
Shorea aptera	95 5	51	55	268	...	Heim
Teglam fat	95·3	51	55	256	...	"
"	95 2 [1]	51	56	277	32 7	Brooks
Commercial samples	95 7	53 5·54	...	283·7		Geitel
"	...	52	53 5	273 5	31 5	Sachs

[1] Unsaponifiable matter, 0·5 per cent.

Enkabang fat obtained from the fruit of *Shorea gysbertiana*, a large tree growing freely in Sarawak, is prepared by the natives by the dry process, *cp.* p. 600. The fruit contains 31·2 per cent of fat and the air-dried kernel 46·7 per cent. *Brooks*[1] examined a fat of native manufacture and also one extracted with carbon bisulphide. The figures are given in the following table. The fat is used as a food by the Dyaks.

	Native Fat.	Extracted with Carbon Bisulphide.
Oil—		
Specific gravity at 100° C. (water at 15·5° 1)	0·854	0·856
Melting point, ° C. .	34·43	33·37
Saponification value	190·2	190·8
Iodine value	30	30
Butyro-refractometer at 40° C., " degrees "	45	16·1
Fatty Acids—		
Insoluble acids + unsaponifiable, per cent .	.	96·4
Unsaponifiable matter	.	0·3
Solidifying point .	.	53
Melting point .	.	55·5
Iodine value .	.	31
Mean molecular weight .	..	282

Borneo tallow has a light green colour, changing to yellow, and after prolonged exposure to the air, to white. At the ordinary temperature it resembles cacao butter in consistence, as also in taste. It has a crystalline, granular structure, and is covered with fine white needles of stearic acid, the quantity of which amounted, in the case of the specimen examined by *Geitel*, to 9·5-10 per cent. This specimen commenced to melt at 35-36° C., and liquefied completely at 42° C. The solidifying point of the insoluble fatty acids was 53·5-54° C.; they consisted of 66 per cent of stearic and 34 per cent of oleic acids. The somewhat low solidifying point of the mixed fatty acids would seem to indicate the presence of palmitic acid. The probable iodine value of the fat, calculated from the last given figure, is about 31. Borneo tallow is therefore placed next to kokum butter.

By crystallising Borneo tallow from acetone *Klimont*[2] obtained the mixed glycerides oleodistearin and oleodipalmitin.

Borneo tallow is employed by the natives for edible purposes; in Manila it is used for the manufacture of candles. It is exported to Europe, and should prove a valuable material for soap- and candle-making. The statements that it is also used for " stiffening " edible cocoa nut oil (*Fritzweiler*), and for adulterating cacao butter (*Sachs*), require confirmation.

The seeds from a plant growing wild in Sumatra, and identified as *Skaphium lanceatum*, Mig. (*Xanthophyllum lanceatum*, Smith), native name " Sioer," yield on extraction with ether 39 per cent of a greenish-

[1] *Analyst*, 1909, 206.
[2] *Monatsh. f. Chem.*, 1904, 929. •

yellow fat, similar in its properties to tankawang fat. The seeds contain a poisonous saponin; hence they cannot be used for feeding stock. The extracted fat had the following characteristics, according to *Gorter* :—

Fat—

Saponification value	198 5
Iodine value	36 6
Acid value .	12 2

Fatty Acids—

Solidifying point .	51 5
Melting point	51 0
Mean mol. weight .	268

Cocoa Nut Oil Group

The fats belonging to the cocoa nut oil group differ from most other vegetable fats by their high saponification values These are due not only to a large amount of lauric acid, but also to a certain proportion of volatile acids, amongst which the "water-insoluble" acids predominate. Hence these fats are characterised by high *Reichert-Meissl* values.

The considerable proportion of volatile acids which the fats belonging to this group contain brings them into relationship with the milk fats of the mammals, but they differ from the latter essentially, not only with respect to their vegetable origin (and consequently by the presence of phytosterol as against cholesterol in the milk fats), but also in that they do not contain *butyric* acid It is due to the proportion of volatile acids in the members of this group that they can be differentiated from other vegetable fats, which contain considerable amounts of lauric acid, and which, therefore, are also characterised by high saponification values (These latter fats are comprised in a separate group, the most prominent member of which is dika fat. See " Dika Fat Group.")

Owing to their peculiar chemical composition (simulating to some extent that of butter fat) these oils are not readily saponified by weak caustic lyes. They require for saponification alkaline lyes of high strength, and are thereby so easily converted into soap that it is only necessary to stir the fats and caustic alkali together at 30-35° C., and allow the mixture to stand. After some time saponification will take place with liberation of heat. (*Soap-making by the cold process.*) The soaps thus formed are very hard, and combine with a large amount of water without becoming soft. These soaps have further the remarkable property of requiring large quantities of salt to throw them out of their aqueous solution, hence they are used as " *marine soaps.*"

The following fats—arranged in the order of their iodine values —are included in this group :—

(a) Muriti fat.
(b) Mocaya oil.
(c) Cohune oil.
(d) Areca nut fat.
(e) Maripa fat.
(f) Aouara kernel oil.
(g) Palm kernel oil.
(h) Cocoa nut oil.
(i) Fat from *Cocos acrocomoides*.
(j) Tonka butter.

(a) MURITI FAT [1]

French—*Huile de Muriti.* German—*Muritifett.*
Italian—*Burro di Muriti.*

Muriti fat is obtained from *Mauritia vinifera*, Mart. (*Acrocomia vinifera*, Oerst.), a South American palm. The seed kernels are slightly roasted by the natives, ground to a paste, then slightly warmed by exposing to steam escaping from boiling water, and expressed in sacks between warmed iron plates. The fat has a pleasant taste, and is similar to cocoa nut oil.

Physical and Chemical Characteristics of Muriti Fat

Specific Gravity at 25° C.	Melting Point. ° C.	Solidifying Point. ° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.
0·9136	25	17	246·2	25·2	5

The specimen examined by *Fendler* [1] was prepared from a Nicaraguan fruit which yielded 48·7 per cent of fat, having an acid value of 1·69. The melting point of the fatty acids, obtained from three specimens, was 54·5° C.; it is therefore likely that the fat contains myristic acid.

The statement that this fat is also prepared in Trinidad, Jamaica, and Brazil, and has an odour of violets and a sweetish taste, requires confirmation, and seems to be due to confusion with ordinary palm oil. This opinion of the author is confirmed by the further statement that this fat is sold in the localities named as palm oil (cp. "Aouara Oil," p. 614).

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1903, 1025.

(b) MOCAYA OIL,[1] MOCAYA BUTTER, MACAJA BUTTER

French—*Huile de mocaya*.   German—*Mocayaol, Macaja butter*.
Italian—*Burro di mocaya*.

Mocaya oil is obtained from the kernels of *Acrocomia sclerocarpa* ;
Mart. (*Cocos sclerocarpa, Cocos aculeata*, Jacq., *Bactris minor*, Gärt.), a
palm tree occurring in Paraguay and forming there vast forests.   The
kernels contain 60-70 per cent of a fat, which greatly resembles cocoa
nut oil in its colour, odour, and consistence.

The oil is known in Trinidad under the name of "Gru-gru" oil.[2]

Sack[3] describes this fat under the local name "kaumakka," and as
originating from the Surinam maccasuba palm (*Acrocomia sclerocarpa*,
Mart.).   According to *Sack* the kernels yield only 24·8 per cent of
fat, melting at 32·5° C.   The fatty acids are stated to consist of 17·5
per cent of oleic and 82·5 per cent of lauric acids.   Evidently *Sack*
has overlooked the occurrence of volatile fatty acids.

The fat from *Acrocomia totai* Mart. appears to be very closely allied
to Mocaya oil.   The kernels yield 58·9 per cent of a light yellow oil
having a pleasant taste.   The following characteristics were given
by *Grimme* :—

Solidifying point. ° C.	Saponification Value.	Iodine Value	Refractive Index.		Unsaponifiable Matter. Per cent.	Observer
			° C.	nD.		
8	188 3	26 9	25	1·4580	13·4	Grimme

Solidifying Point. ° C.	Neutralisation Value.	Mean Molecular Weight.	Iodine Value.	Refractive Index.		Observer.
				° C	nD.	
28-30	191·4	293 4	29·3	30	1·4460	Grimme

These figures stand in need of confirmation.   As the saponification
value of the fat, and the mean molecular weight of the fatty acids
are much too low for the fats belonging to this group, doubt is thrown
upon these figures by the low proportion of insoluble fatty acids, viz.
92·85 per cent found by *Grimme*.[4]

[1] De Negri and Fabris, *Giorn. farmac.*, 1896, No. 12 ; *Chem. Revue*, 1897, 82.
[2] Knapp, *Journ. Soc. Chem. Ind.*, 1914, 9.
[3] "Inspectie van den Landbouw in West Indie," *Bulletin*, No. 5, 1906.
[4] *Chem. Revue*, 1910, 156.

Physical and Chemical Characteristics of Mocaya Oil

Specific gravity At °C.	Solidifying Point °C	Melting Point °C	Saponification Value Mgrms KOH	Iodine Value	Reichert-Meissl Value c.c. 1/10 norm. KOH	Insoluble Volatile c.c. 1/10 norm. KOH	Acid Value	Observer
99 (water at 15.5=1) 0.861	22	24.29	240.6	24.63	7.0			Sack
100 (water at 15=1) 0.868		26.8	243.5	19.4	7.2	13.9	1.2	Knapp
			255	16.21	5.7-6.8	10.0-12.6	1.5	Imp. Inst.

Physical and Chemical Characteristics of Insoluble Fatty Acids

Solidifying Point °C	Melting Point °C	Neutralisation Value Mgrms KOH	Mean Mol. Weight	Iodine Value	Observer
22.20	23-25	254			Sack
23.05 (Titer test)	24.0	262	214	19.7	Knapp
20.5 (Titer test)					Imp. Inst.[1]

[1] Bull. Imp. Inst., 1913, 559.

(c) COHUNE OIL

French—*Huile de cohune.*   German   *Cohunenussol.*
Italian—*Olio di cohune*

For table of characteristics see p. 610.

This oil is obtained from the kernels of the cohune palm, *Attalea cohune*, Mart., which grows abundantly in British Honduras, Guatemala, and Mexico.[1] The nuts are known in Guatemala as " Manacca Nut."

The kernels have the appearance of small cocoa nuts ; their size is not greater than that of large nutmegs. They contain 40 per cent of a solid yellow fat, resembling in general appearance palm nut and cocoa nut oils.

The mixed fatty acids melt between 27° and 30° C. Five samples examined at the Imperial Institute yielded 65·4-71·6 per cent of a solid white fat. The outer fibrous layers of the fruit contained 9 3-20 6 per cent of a greenish-yellow fat, of which the following characteristics were determined [2]. ·

Specific gravity at 100/15 5° C	0 848
Saponification value .	197 4
Iodine value .	75 1
Reichert-Meissl value	1 65
Acid value .	162 0
Unsaponifiable matter, per cent	0 95
Insoluble acids + unsaponifiable	97 0
Solidifying point, ° C.	31·0

Owing to the extreme hardness of the husks, the commercial exploitation of the cohune nuts, which are readily obtainable in large quantities, has hitherto not been taken in hand.

It is doubtful whether the fat from the kernels of the Surinam *Bactris plumeriana*, Mart. (German— *Affendornfett*), known under the native name " keekeesiamakka," and described by *Sack*,[3] is identical with cohune oil. The kernels are stated by *Sack* to contain 31·8 per cent of a fat melting at 32° C., the fatty acids of which are said to consist of 13 6 per cent of oleic and 84·6 per cent of lauric acids. It will be observed that in this case also no mention of volatile fatty acids is made by *Sack*.

[1] *Bull. Imp. Inst.*, 1903 (xxv.).
[2] *Bull. Imp. Inst.*, 1913, 226.
[3] " Inspectie van den Landbouw in West Indie," *Bulletin*, 1906 (5).

[Table

Physical and Chemical Characteristics of Cohune Oil

Specific Gravity		Solidifying Point °C.	Melting Point °C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Insoluble Volatile Acids.	Observer.
At °C.	100° (water at 15·5=1)							
..		16·15	18·20	253·9-255·3 [1]	12·9-13·6	..	..	Sack
	0·868-0·871 [2]	..	..	252·4-256·5	11·0-13·7	6·8-8·3	12·5-15·4	Imp. Inst. [2]

[1] The original stated erroneously saponification "equivalent" instead of saponification "value."

[2] The unsaponifiable matter 0·23-0·28 per cent, and insoluble acids + unsaponifiable 87·7 per cent.

(d) ARECA NUT FAT

This fat was obtained from the nuts of *Areca catechu*, L., by extraction. The colour as also the composition of the fat varies with the solvent used, as is evidenced by the data given in the following table :—

	Fat extracted with Ether.	Fat extracted with Petroleum Ether.
Fat—		
Colour	Reddish-brown	Yellowish-white
Odour	Like nutmeg	Nearly odourless
Specific gravity	0·884	0·973
Melting point	36°·37° C.	37°·38° C.
Saponification value	227·4	234·6
Iodine value	24·3	12·3
Reichert-Meissl value	0·2	4·2
True acetyl value	11·2	9·81
Unsaponifiable matter	1·12 per cent	1·01 per cent
Acid value	91·1	97·2
Fatty Acids—		
Fatty acids + unsaponifiable	92·76 per cent	91·45 per cent
Melting point	39° C.	39°·40° C.
Mean molecular weight	244·6	238·5
Iodine value	25·95	13·6

According to *Rathje*,[1] the fatty acids obtained from the two fats have the following compositions :—

	Fat extracted with Ether.	Fat extracted with Petroleum Ether.
	Per cent.	Per cent.
Stearic acid	2·25	3·3
Palmitic acid	3·1	2·5
Myristic acid	21·0	24·7
Lauric acid	43·7	53·3
Capric acid	1·0	1·0
Caprylic acid	..	Small quantity
Caproic acid	..	Small quantity
Oleic acid	29·0 (?)	14·5

In the author's opinion the fat extracted with petroleum ether would correspond best in its composition with the other fats belonging to the " Cocoa Nut Oil Group."

[1] *Arch. d. Pharm.*, 1908, 702. .

(e) MARIPA FAT [1]

French—*Huile de maripa.*   German—*Maripafett.*
Italian—*Sego di maripa.*

For tables of characteristics see p. 613.

Maripa fat is obtained from the kernels of *Palma (Attalea) maripa,* Aubl., a plant belonging to the palm family. This palm is indigenous to the West Indies. In Brazil the nuts known as Urukuri nuts are used in the curing of rubber. Probably the commercial fat is also obtained from one or two other species of *Attalea,* viz. *A. excelsa,* Mart. *(Maximiliana maripa,* Drude) and *A. spectabilis.* The fat is prepared by expression or, in a cruder fashion, by boiling the fruit with water, when the fat rises to the top and is skimmed off. The expressed fat is colourless or faintly yellow ; it has a mild taste and a faint, not unpleasant odour.

Maripa fat is used as an edible fat in the West Indies and French Guiana ; it is also used in pharmacy.

The fatty acids from the fat of *Attalea excelsa* are stated by *Frank and Gnädinger* to consist chiefly of caproic, caprylic, and capric acids. They also state that they found small amounts of butyric acid.[2] The fat from *Attalea spectabilis* examined by *Grimme* [3] had the acid value 8·1, and contained 1·08 per cent of unsaponifiable matter. Although the Reichert-Meissl value was not determined it would probably lie somewhere in the neighbourhood of 7-8.

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[1] Van der Driessen Mareeuw, *Nederl. Tijdschr. Pharm. Chem. en Toxicologie,* 1900 (12), 245 ; *Pharm. Weekblad,* 1905 (46), 948.
[2] *Gummi-Zeit.,* 1910, 1328.   [3] *Chem. Revue,* 1910, 233.

Physical and Chemical Characteristics of Maripa Fat

Specific Gravity. At °C.	At 100° C. (water 15·5=1.)	Solidifying Point. °C.	Melting Point. °C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Reichert-Meissl Value. c.c. 1/10 norm. KOH.	Refractive Index. At °C.	"D.	Observer.
At 100° C. (water 15·5=1.)	0·8686	24·25	26·5·27	270·5	17·35	4·45	..	..	v. d. Driessen Mareeuw
11	0·9012	16·17	23 18·19	259·5 348·3·349	9·49 16·15·7	10·5	..	..	Bassière[1] Frank and Gnadinger[2]
30	0·8692	23·0	24·5	236·6	3·6	..	30	1·4527	Grimme[3]

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.	Specific Gravity. At 100° C. (Water 15·5=1).	Solidifying Point. °C.	Melting Point. °C.	Iodine Value.	Mean Molecular Weight.	Refractive Index. At °C.	"D.	Observer.
88·88	0·823	25	27·5·28·5	17·4	..	..	..	v. d. Driessen Mareeuw
93·53	..	36·5	38·5	8·8	218·7	60	1·4304	Grimme

1 Journ. Soc. Chem. Ind., 1903, 1137.   2 Oil from Attalea excelsa.   3 Oil from Attalea speciabilis.
4 Private communication from v. d. Driessen-Mareeuw.

(f) AOUARA KERNEL OIL

French—*Huile d'amande d'aouara.* German—*Aouarakernöl.*
Italian—*Olio di noci di aouara.*

This oil is obtained from the kernels of the aouara palm fruit (p.. 532). The kernels yield 46 per cent of a whitish solid fat of pleasant odour. The natives prepare the fat by pounding the kernels and boiling the mass with water; the skimmed-off fat is known locally under the name "quioquio" or "thiothio." The fat prepared by *E. Bontoux*[1] from the kernels had the acid value 9·6. The following characteristics were ascertained by him :—

Fat—

Solidifying point	.	.	.	.	26·2° C.
Melting point	.	.	.	.	29·30° C.
Saponification value	.	.	.	242·5-243 3
Iodine value	.	.	.	.	10·4-11·2

Fatty Acids—

Insoluble fatty acids + unsaponifiable	.	91·7 per cent
Neutralisation value of fatty acids	.	248·4-249 8
Mean molecular weight „	.	225

In Guiana "quioquio" fat is used for medicinal and edible purposes.

(g) PALM KERNEL OIL, PALM NUT OIL

French—*Huile de palmiste.* German—*Palmkernol, Kernöl.*
Italian—*Sego di noce di palma.*

For tables of characteristics see p. 622.

Palm kernel oil is obtained from the kernels of the palm tree fruit (p. 533). The palm fruit contains, as a rule, only one kernel; seed from West African palms planted in Amani, German East Africa, furnished, however, many fruits containing two kernels.[2] The proportion of oil in the kernels was also very small, 33-37 per cent, when compared with the yield of oil from West African kernels. The kernels are collected by the natives after the palm oil has been recovered from the fleshy part of the fruit; the shells are removed by cracking each nut separately with a stone or hammer. This work is chiefly done by women and children. Owing to the laboriousness of this process, and also owing to the facts that no more than about fifteen pounds of kernels are obtained by one worker in a day, and that the kernels have to be carried to the market, enormous quantities of palm nuts are

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[1] Lewkowitsch, *Technologie et analyse chimiques des huiles, graisses et cires,* vol. ii. 1104.

[2] Cp. Lommel, *Der Tropenpflanzer.*

wasted.[1] The kernels are collected at the coast stations and shipped to Europe. The chief receiving ports are Hamburg, Liverpool, and Marseilles.

The first palm kernels that came to Europe were brought to Marseilles as ships' ballast from the French West African colonies early in the 'fifties of the last century, and were thrown into the sea as soon as the ship was again to be loaded. An enterprising oil miller in Marseilles recognised the value of the kernels, and commenced the manufacture of palm kernel oil.

Recently several machines have been constructed for the breaking of the kernels on the spot, but in view of the exceedingly cheap labour (of women and children) in West Africa, it has yet to be seen whether the machines will meet with extended application in the near future. One of these was tested at the Government Botanic Gardens, Aburi, and it was ascertained that by using it the cost of labour was reduced by about 42 per cent. But, at the same time, over 20 per cent of the nuts passed through the machine unbroken. *Haake's* machine has been also tried (see " Palm Oil," p. 534), but according to reliable information given to the author it has not proved successful. The problem of expeditiously cracking the nuts in Africa is, therefore, still an unsolved problem, which must approach its solution in the future, as the opening up of the country by railway lines, and the increased facilities of transport by water, will assist in emphasising the enormous waste that is being incurred at present. It has also been attempted to express palm kernel oil on the spot,[2] but the presses were too heavy to be worked by women and children, and therefore fell into disuse. In this connection the author may state that it would hardly pay under present circumstances to extract the oil on the spot, as the residual cake, forming about 50 per cent of the kernels, has a high value in Europe, whereas it would be perfectly valueless in West Africa. The quantities of palm kernels that are imported into Europe are given in the following table :—

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[1] Nut-cracking machines have been made by *Miller* and by *Haake*, but hitherto they have not been able to supplant manual labour. Cp. also S. C. Phillips, English patent 9733, 1907.

[2] Cp. J. Ambleston, English patent 20185, 1904.

Imports of Palm Kernels into Hamburg, Liverpool, and Marseilles

Year.	Imported into Hamburg.	Imported into Liverpool.	Imported into Marseilles
	Tons.	Tons	Tons.
1875	...	...	1,796
1880		.	2,760
1885	.		20,288
1890	...	.	28,864
1895	...	. .	13,385
1896	101,537	.	19,667
1897	88,707	.	12,967
1898	101,083	.	10,953
1899	106,208	. .	7,685
1900	117,987	...	8,287
1901	132,005		8,893
1902	160,099	32,404	8,096
1903	152,078	25,446	4,628
1904	159,118	26,500	7,514
1905	156,708	22,000	3,552
1906	151,105	25,280	4,170
1907	188,019	23,450	4,412
1908	193,468	20,226	1,675
1909	235,616	17,206	3,639
1910	256,668	23,826	1,262
1911	280,429	20,799	1,832

The chief centre of the palm kernel oil industry is Harburg (near Hamburg), whence most of the palm kernel oil used in England is shipped. The following table shows the imports of palm kernel oil:—

Palm Kernel Oil imported into Liverpool

Year.	Tons.
1900	3,892
1901	4,744
1902	15,004
1903	8,448
'1904	14,438
1905	11,292
1906	7,128
1907 (year of high prices for oils)	14,658
1908	6,962
1909	9,690
1910	5,439
1911	1,722
1912	1,998

At present considerable quantities of palm kernel oil are being produced in Liverpool.

Details of German trade in palm kernel oil are given in the following table :—

Imports.			Exports.		
From	1911.	1912.	To	1911.	1912.
Belgium	..	3	Belgium	733	779
United Kingdom	128	3	Denmark	613	323
			United Kingdom	11,837	5,879
			Holland	374	433
			Austria-Hungary	6,944	6,428
			Finland	397	338
			Switzerland	1,389	1,616
			United States of America	14,911	15,826

The total annual production of palm kernels in the French colonies reaches about 30,000 tons per annum. The following table gives some details :—

Exports of Palm Kernels from the French Colonies

In metric tons

Year.	Senegal.	French Guinea.	Ivory Coast.	Dahomey.	French Congo
1900	430	2385	3108	21,986	688
1901	733	2103	2982	24,212	611
1902	481	2894	3417	29,778	728
1903	772	2819	2840	21,685	621
1904	903	2855	3366	25,997	691
1905	903	2810	3169	17,480	667
1906	1045	2930	3217	18,835	442
1907	1431	3748	3351	18,810	...
1908	1517	3509		24,035	389
1909	1191	3762	5191	35,224	375
1910	1439	4579	5422	34,783	577

The imports of palm kernels into Marseilles have decreased considerably during the last ten years, and at present kernels are only occasionally expressed there. This is due to the cake not finding a ready sale as cattle food in the South of France, the cocoa nut cake having almost completely ousted the palm kernel cake from that market. In fact, the small quantities of cakes that were prepared in the Marseilles market were extracted with carbon bisulphide, to recover the whole amount of oil; hence the extracted cakes had only value as manure. (At present the extraction of palm nut cake with solvents has been abandoned in Marseilles as being unremunerative, but is still continued on a large scale in Hamburg. An apparatus for the extraction with benzene has been patented by *Diehm and Knolle*.[1]

[1] German patent 262,194.

The small quantities that are made in Marseilles are sold as cattle food.) In Germany, on the other hand, palm kernel cakes find a ready outlet as food for young pigs.

The kernels are screened to free them from shells, stones, nails, and hammerheads, passed over magnetic separators, and then ground between rollers to a paste. The pulpy mass is either expressed in hydraulic presses or extracted with solvents. In the first process the meal must be pressed twice, on account of the large proportion of fat the kernels contain.

On a commercial scale the first expression of palm kernel meal is carried out at a temperature of 45-50° C., the second at 55-60° C. Thus 43-45 per cent of palm kernel oil is recovered.

The press cake contains 6-8 per cent of oil; its proportion of nitrogen is small (about 2·5 per cent); hence its value as cattle food is somewhat low. For the same reason the extracted meal has little manurial value.

The variations of the percentage of oil in the kernels will be gathered from the following two tables. The first table, due to *Fendler*,[1] refers to the varieties of palm fruits described above (p. 537).

Variety	Oil Per cent.	Moisture. Per cent.
De	43·7	8·2
De de bakni	49·1	6·5
Se de	49·2	5·9
Afa de	45·5	6·5
Small-fruited Lisombe	49·2	...
Large-fruited Lisombe, ripe	48·9	..
Large-fruited Lisombe, unripe	49·2	...

The numbers given in the following table, due to *Nördlinger*,[2] refer to commercial brands of palm kernels :—

Origin of Palm Kernels.	Proportion of Fat. Per cent.	Origin of Palm Kernels.	Proportion of Fat. Per cent.
Sierra Leone	48 6	Togo District, French	49·3
Island of Sherboro	46·7	Lagos	50 4
Liberia	49·4	Benin	49 8
Grand Bassa	50·2	Niger	50 5
Half Jack	50·8	Brass	52·5
Apollonia	47·2	Calabar	50·9
Dixcove	48·2	Bonny	51 0
Cape Coast Castle	50 2	Opobo	52·3
Winnebah	46·1	Cameroons	49 0
Quitta	48·4	Congo	47·4
Togo District, German	52·1	Loanda	50·9

[1] *Berichte d. Pharm. Ges.*, 1903, 115.
[2] *Journ. Soc. Chem. Ind.*, 1895, 585.

The colour of palm kernel oil is white to pale yellow. In the fresh state the oil is neutral and has a pleasant smell and an agreeable nutty taste. Commercial samples contain, however, notable amounts of free fatty acids. The following table gives the proportions found in various samples of palm nut oil :- -

Free Fatty Acids in Palm Kernel Oil

Kind of Oil.	No. of Samples.	Free Fatty Acids as Oleic Acid.	Observer.
		Per cent	
Expressed oil	27	3 30-17 65	Nördlinger
,, ,,	2	9 8 -11·16	Emmerling
,, ,,	6	2 6 - 6·2	Lewkowitsch
Extracted oil	10	4·17-11·42	Nördlinger
,, ,,	5	6 38- 8·69	Emmerling
,, ,,	4	3 29- 4·13	Fendler

Emmerling [1] found the following increases in the amounts of free fatty acids in some specimens of oil kept in closed bottles for two years :—

Sample No	Free Fatty Acid calculated as Oleic Acid.	
	Fresh Oil	After Two Years.
	Per cent.	Per cent.
1	7·39	9 25
2	6 38	8·59
3	7 54	8·74
4	9 80	11 86

On exposure to the air for four months the amount of free fatty acids increased but little, viz.—from 8·59 and 8·74 to 9·10 and 10·00 per cent respectively; whilst the amount of volatile fatty acids, measured by the *Reichert-Meissl* value, increased after four months' exposure to the light from 5·96 and 5·41 to 6·69 and 6·38. The same samples kept in the dark showed after the same time 7·28 and 6·53 respectively.

The iodine values also decreased on keeping in closed bottles, as shown in the following table :—

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[1] *Landw. Versuchsst.*, 1898, 51.

Sample No.	Iodine Value.	
	Fresh Oil.	Oil kept Two Years in Closed Bottle.
1	16·23	11·28
2	16·76	10 06
3	15·37	10·56
4	15·30	11 94

Palm kernel oil dissolves completely in four volumes of absolute alcohol at 32° C. (*Milliau* [1]).

The chemical composition of palm kernel oil is not fully known.

Valenta [2] examined the mixed fatty acids. By passing a current of steam through the acids a small quantity volatilised; the distillate consisted of *caproic* acid, and most likely also of *caprylic* acid. After drying the acids that remained behind and distilling them fractionally, at a pressure of 100-160 mm., six fractions were obtained, the examination of which led to the results recorded in the table :—

Fraction No.	Boiling Point	Melting Point.	Saponlf. Value.	Iodine Value.	Yield.	Saturated Fatty Acids.	Oleic Acid	Constituents of the Fraction
	° C.	° C.			Per cent	Per cent.	Per cent.	
1	185-190	..		0	4	100	0	Caprylic, capric
2	190-200	31·5	310	2 6	10	97 2	2 8	Capric, oleic
3	200-205	37·5	275	3 4	58	96 3	3 7	Lauric, capric, oleic
4	205-225	32 5	264	7 8		91 5	8 5	„ „ „
5	225-245	31 5	251	16 7	15	81·7	18 5	Lauric, myristic, oleic
6	245-270	35 0	219	41 3	5	54 6	45 3	Myristic, palmitic, oleic
7	Residue	..	..	..	8	..	..	

A number of experiments made in the author's laboratory yielded insoluble volatile acids (*Polenske* method) 10-12.

The volatile fatty acids of a specimen of palm kernel oil having the (very high) acid value 34, *Reichert-Meissl* value 5·2, and the number for insoluble volatile acids (see "Butter Fat") 9·3, were examined by *O. Jensen*, [3] who states that *butyric* acid was absent, and that the amounts of deci-normal alkali required for caproic, caprylic, and capric acids for 5 grms. of the palm kernel oil were 2·5 c.c., 1·1 c.c., and 23·0 c.c. respectively (cp. "Cocoa Nut Oil," p. 643).

Elsdon, [4] by following *Haller's* method of alcoholysis (cp. Vol. I. p. 665), resolved the fatty acids of palm kernel oil into the following fractions :—

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[1] *Compt. rend.*, 1892 (115), 517.

[2] *Zeitschr. f. angew. Chem.*, 1889, 335.

[3] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905, 265.

[4] *Analyst*, 1914, 78.

Caproic acid	.	.	2		Myristic acid	.	.	12
Caprylic acid	.	.	5		Palmitic acid	.	.	9
Capric acid	.	.	6		Stearic acid	.	.	7
Lauric acid	.	.	55		Oleic acid	.	.	4

The amount of oleic acid appears to be too low.

The chief constituent of palm kernel oil is therefore lauric acid. From the iodine value the author calculates the proportion of oleine as 12-20 per cent. The older statement of *Oudemans* that palm kernel oil contains 26·6 per cent of oleic acid, must be abandoned as erroneous. Palm kernel oil is very nearly related in its chemical composition to cocoa nut oil. Like the latter it is remarkable on account of its high saponification value, and the notable amount of glycerides of volatile fatty acids it contains (cp. "Cocoa Nut Oil," p. 643). It also requires, like cocoa nut oil, strong caustic soda lye for saponification, and yields a hard white soap, which is only thrown out in the "salting out" process by a large amount of salt.[1]

Palm kernel oil is largely used for soap-making, chiefly in admixture with other oils and fats. Like cocoa nut oil it is eminently suitable for the manufacture of soaps by the cold process. The freshest oil is employed in the manufacture of vegetable butter (like "Cocoa Nut Oil" (p. 648)), and of "Chocolate Fat."

In this latter manufacture a hard fat ("*palm nut stearine*") is obtained; the liquid "*palm nut oleine*," being a by-product, is used in soap-making. A sample of palm nut oleine, examined by the author, had the titer test 16·8-17° C.

Palm nut oil is not adulterated with other fats (cp. also p. 648). The edible variety of palm nut oil is, however, used for adulterating butter fat and cacao butter (see p. 587).

[1] Cp. Lewkowitsch, *Journ. Soc. Dyers and Colourists*, 1891, March; *Journ. Soc. Chem. Ind.*, 1894, 258.

	Specific Gravity		Solidifying Point		Melting Point		Saponification Value		Iodine Value		Reichert-Meissl Value		Refractive Index	
°C	°C	Observer	°C	Observer	°C	Observer	Mgrms. KOH	Observer	Per cent	Observer	c.c. norm. KOH	Observer	At 60° C.	Observer
40 (water at 15.5=1)	0·9119	Allen	23·03	Feudler	23-28	Valenta	247·6	Valenta	10·3-17·5	Valenta	5·0	Lewkowitsch	1·4431	Thorner
90 (water at 15.5=1)	0·8731	,,	24·04	,,	25-26	Thorner	246-230	Thorner	13·4-13·6	Morawski and Demski	5·41-	Enmerling		Butyro-refractometer
			23·05	,,	30·03	Feudler	242·4-244·1	Lewkowitsch	18·14	Thorner	5·95	lung		
			24·08		25·54	,,	21·91	Enmerling	15·4-16·87	Enmerling	5·85·4	Fendler	At 40° C.	
					29·5	,,	254·82	Fendler	14·93	lung	6·34·4	,,	"Degrees."	
					29·6		248·83	,,	16·84	Fendler	6·22·5	,,		
							249·4	,,	15·65		6·82·6	,,		
							250·05	,,	15·46				36·5	Beckurts and Seiler
							246·38				7·6	Menon		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Solidifying Point		Titer Test.	Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
Per cent.	Observer	°C.	Observer	°C.	°C.	Observer	Mgrms. KOH.	Observer		Observer	Per cent	Observer	At 60° C.	Observer
91·1	Lewkowitsch	20·0-20·5	Lewkowitsch	20·7	25-28·5	Valenta	258-265	Valenta	211	Valenta	12·07	Morawski and Demski	1·4310	Thorner
		22·5-24·5			20·7	Thorner	264	Thorner	222·8	Lewkowitsch	12	Thorner		
		23·5-24·5					2317	Lewkowitsch				Liquid Acids.		
		24·6-25·5									44-48	Pick 8		

1 Extracted oil.   2 Expressed oil.
3 From De palm   the oil contained 54·05 per cent free fatty acids (calculated to oleic).
4 ,,   De de bakrul palm   ,,   55·07   ,,
5 ,,   Se de palm   ,,   55·38   ,,
6 ,,   Afa de palm   ,,   57·18   ,,   ; op. p. 619.
7 After keeping for two years in closed bottles these values had decreased ; op. p. 619.   8 Determined in the author's laboratory.

(h) COCOA NUT OIL

French—*Beurre de coco* ; *huile de coprah.* German—*Kokosöl* ;
Kokosnussöl. Italian—*Burro di cocco.*

For tables of characteristics see pp. 645-647.

Cocoa nut oil is the fat obtained from the kernels of the cocoa nut,
especially from those of the two species *Cocos nucifera*, L., and *Cocos
butyracea*, L.

Cocos nucifera grows on all coasts and islands of the tropics ; in
fact, it may be considered a cosmopolitan of all tropical coast lines in
both hemispheres.

De Candolle is of the opinion that the cocoa nut tree is indigenous
to the Islands of the Malayan Archipelago, whence the nuts were driven
by the sea currents towards the East to the Pacific Islands and the
coasts of Central America, and towards the West to Ceylon and the
east coast of Africa.[1]

The fruits falling into the sea are carried by the waves into distant
countries, and the seed, being well protected by the " coir " (fibres),
is able to germinate on all shores (islands and even coral reefs) where
the fruits may be deposited. The tree grows best in the neighbourhood
of the coast and a few miles inland at low altitudes. It will also grow
far inland,[2] but there it no longer bears fruit ; nor does it bear fruit
in sub-tropical climates. It forms large forests, especially on the
coasts of Ceylon, Java, and the Philippines. On account of its mani-
fold uses, the tree has been cultivated early in the history of mankind,
and the fruits were therefore gathered, so to speak, on a commercial
scale, not only in the localities named, but also in all South Sea Islands,
Madagascar, Mauritius, Ceylon, Zanzibar, the East and West Coasts
of Africa, the Antilles, and the coast lines of tropical South America.

According to the *Cocoa Nut Planters' Manual*, the area under culti-
vation for cocoa nut palms in 1907 was as follows :—

	Hectares.	Acres.
Ceylon	330,525	750,000
South America	202,350	500,000
India	161,880	400,000
Straits Settlement, Philippines . . .	141,645	350,000
Java, Sumatra	101,175	250,000
South Sea (Pacific Islands)	105,200	260,000
Mauritius, Seychelles, Madagascar, Zanzibar,		
Réunion, and East African Coast . .	44,517	110,000
Siam and Cochin China	40,470	100,000
West Indies	44,517	110,000

[1] Hubert, *Le Cocotier*, Paris, Dunod and Pinat, 1906.
[2] Cocoa nut trees grow at Luang-Prabang, in Indo-China, a distance of about 100
miles from the sea.

Cocos butyracea is indigenous to Brazil, and yields, together with *Cocos nucifera* (and all the other species of the *cocos* family mentioned already, such as *Cocos sclerocarpa*, etc.), the chief quantities of cocoa nut fats that are consumed locally. The exported cocoa nut oil is, however, mainly derived from *Cocos nucifera*.

The cocoa nut tree flowers when about 6 or 7 years old, and begins to bear fruit fully when it has reached the age of about 8 to 10 years. It then retains its fertility up to an age of 60 years and more, and under favourable conditions (as regards soil and moisture) it even bears fruit up to the age of 100 years. The cocoa nut palm, when in full vigour, produces about sixty nuts annually. The nuts contain a fleshy endosperm built up from a milky juice rich in oil. At the period of maturity of the fruit the milky juice has disappeared almost completely, and the endosperm forms the well-known cocoa nut kernel ("cocoa nut meats"), inside which the remainder of the milky juice —cocoa nut milk—is enclosed.[1] The kernel contains from 30 to 40 per cent of fat, and about 50 per cent of moisture. One thousand nuts yield about 200-250 kilos. of dried kernel (containing on the average about 10 per cent of moisture), which is known under the name of copra.

Since the earliest time in the history of mankind, the kernels have been used by the natives of the South Sea Islands, and especially of India, as one of their chief articles of food. The mode of preparing the oil, as practised centuries ago, would therefore hardly have differed from the primitive methods described in the foregoing pages for the preparation of other fats, such as palm oil, carapa oil, etc. Thus on many South Sea Islands the kernels were cut into small pieces and exposed in piles to the sun, when the oil would run off spontaneously. An improvement on this method consisted in converting the kernels into pulp, placing the latter in vessels perforated with holes, and exposing them to the sun, when the oil would run through the holes. The oil was then collected and carried in bamboo sticks to the market, a method which is still being practised nowadays, or has been practised up to a few years ago, in the outlying parts of the Philippines.[2]

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[1] Recent analysis by A. Behre (*Pharm. Zentralbl.*, 1906, 145) of the cocoa nut milk from three Ceylon cocoa nuts gave the following results :—

Specific gravity at 15° C.	1·0214	1·0269	1·0325
100 c.c. contained—			
Water	91·20	93·55	92·25 grms.
Extract	5·797	6·447	7·746 ,,
Ash	0·665	0·802	1·000 ,,
Proteids	0·811	0·300	0·441 ,,
Fat	..	0·015	0·014 ,,
Phosphoric acid as P_2O_5	0·051	0·103	0·182 ,,
Chlorine	0·158	8·220	0·221 ,,
[a]D in 200 mm. tube before conversion	+3° 28′	+4° 12′	+5° 10′
,, ,, ,, after conversion	−1° 8′	−2° 1′	−2° 25′

Cp. also E. de Kruyff, *Bullet. du Départ. de l'Agric. aux Indes Néerland.* iv. 1907.

[2] Practically the same process is employed by the natives of Cochin China and Annam, *Bull. éconbm. de l'Indo-Chine*, No. 45, Sept. 1905 ; *Les Principaux Oléagineux de l'Indo-Chine*, Hanoi, 1906.

Further progress was marked by the endeavour of the natives to render their process of manufacture independent of the heat of the sun—as in the rainy season. Thus the kernels were laid on hurdles, formed from bamboo staves and cocoa nut leaves, and dried over a slow fire. The dried kernels were then pounded and subjected to expression in an improvised press (cp. Chap. XIII.).

In India, where cocoa nut oil became at an early date an extensively used food product, and where it not only replaced butter, but was also used for pharmaceutical purposes, more refined methods of preparation were resorted to. The nuts were split into halves by a blow with a sharp instrument, the cocoa nut milk was poured off, and the halves exposed to the sun to dry, when the kernels became readily detachable from the shell. The dried kernels were then triturated, and expressed. A still better product was obtained by throwing the pounded kernels into boiling water, when the oil rose to the top, ready to be skimmed off. The residual mass was used as cattle food (cocoa nut poonac). This process was carried out with special care at Cochin on the coast of Malabar. It has remained in existence to the present day, and the reputation of Cochin cocoa nut oil for best quality has been maintained to this day (see below).

In carrying out the primitive processes sketched above it was found, no doubt accidentally, when owing to a good harvest a surplus of nuts was obtained, that the kernels could be preserved for some time by drying them thoroughly so as to remove the bulk of the water. The absence of a considerable quantity of moisture prevented the setting in of excessive hydrolysis and subsequent rancidity, and at the same time prevented the growth of fungi. It will, therefore, be readily understood that at an early stage of civilisation the production of such dried kernels (" copra ") developed into a manufacturing process.

Cocoa nut oil became first known in Europe in the eighteenth century, but did not find any extended commercial use till the middle of the last century.

The first important consignment of cocoa nut oil appears to have arrived in this country in the second decade of the nineteenth century. The first English patent dealing with cocoa nut oil (" as imported ") dates from 1829 (English patent 5842, by *James Soames* the younger). The first installation for expressing cocoa nut oil in this country from copra (" copperah ") imported perfectly fresh in large iron tanks filled up with cocoa nut oil, appears to have been erected by *W. Tindall,* English patent 9230, 1842. The first patent claiming the manufacture of soap from cocoa nut oil is by *R. L. Sturtevant,* English patent 8870, 1841 ; when its characteristic properties as a soap-making material were fully recognised and rapidly created a great demand for the oil. This demand has since then grown to such an extent (as will be gathered from the statistical tables given below) that almost every part of the tropics is contributing to the supply of cocoa nut oil. And yet the production of this oil is still in its infancy, and strenuous efforts are being made, especially in the West Indies and at the West Coast of

Africa, to increase the production. In commerce three qualities of oil are distinguished : (1) Cochin oil, (2) Ceylon oil, (3) Copra oil.

(1) *Cochin* oil is the finest and whitest quality. As stated already, a considerable amount of Cochin oil was prepared originally at the coast of Malabar by boiling the kernels with water and skimming off the oil. This oil owed its fine quality to the freshness of the kernels. A considerable quantity of " Cochin oil " was also made in crude native mills by expression ; during the latter years modern plant has been introduced into India such as is in vogue in Europe (see Chap. XIII.). Cochin oil being obtained from fresh nuts, remains for a short time only exposed to the air in contact with the putrescible matter of the kernel, and therefore contains only a very small amount of free fatty acids. The author found the proportions varying from 1·5 to 3 per cent, calculated to oleic acid. Of course, other cocoa nut oils prepared from fresh kernels with the same care are equal in this respect to Cochin oil. Hence the name " Cochin " has become a generic term for the finest quality of oil, and we, therefore, find in commerce the commercial brands : Cochin Cochin-China, Cochin Australia, Cochin Mauritius, Cochin South America. Cochin " reutre " " neige " are special qualities of white filtered oil.

The superiority of Cochin oil to Ceylon oil seems to be due to some extent to the better climate, as the Malabar coast enjoys a larger number of dry months than does Ceylon. Hence the kernels can be dried in the sun, whereby a whiter and better flavoured oil is obtained than the Ceylon oil quality. The superiority of Cochin oil is, however, chiefly due to better cultivation of the plant (manuring, pruning, destruction of insects,[1] etc.) and better and cleanlier methods of manufacture. The Cochin oil is also stated to contain a larger amount of " stearine " than the Ceylon oil. But this appears doubtful, and may be due to the larger yield of " stearine " obtainable on a large scale, owing to Cochin oil containing a smaller amount of free acids than do Ceylon oils.

By expressing the kernels in the cold an oil of the solidifying point 13°-12° C., and the melting point 20° C., is obtained. This cold-pressed oil, however, is not a commercial product, being used on the spot as a substitute for butter fat.

(2) *Ceylon* oil is prepared in a similar manner (*i.e.* either by boiling or by expressing) in the plantations of Ceylon. This oil, no doubt owing to a certain want of care on the part of the natives as compared with that exercised by the natives of the Malabar coast, represents a second quality of cocoa nut oil. Ceylon oil contains a higher percentage of free fatty acids than Cochin oil. The author found in the examination of a large number of samples, extending over a series of years, from 5 to 10 per cent of free fatty acids (as oleic). Owing to the changes which the putrescible substances of the kernels have undergone before

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[1] In the East the cocoa nut beetle is now becoming one of the greatest pests of the cocoa nut palm. The ravages effected by this beetle in Rangoon are such that the total disappearance of the tree is feared. In Ceylon special regulations are in force to prevent the spreading of this pest.

expression, Ceylon oil possesses the peculiar acrid taste which a cocoa nut oil of a somewhat pronounced rancid character has acquired. This drawback seems to be gradually disappearing, as, according to private information supplied to the author, there are at present some establishments at Ceylon in which cocoa nut oil is prepared by modern methods, so that it approaches Cochin oil in freshness and low percentage of free fatty acids. The "poonac" is consequently of the same good quality as the Malabar "poonac," and considerable quantities are even exported. The extent to which the cocoa nut oil industry has grown in Ceylon may be gathered from the following tables, giving the values, in rupees, and quantities of the exports of some of the cocoa nut products from Ceylon (cp. also table below, "Exports of Copra") :—

[TABLE

Exports of Cocoa Nut Palm Products from Ceylon (Values)

	1901.	1902.	1903.	1908.	1909.	1910.	1911.	1912.
	Rupees.	Rupees.	Rupees.	Rupees.	Rupees.	Rupees.	Rupees.	Rupees.
Cocoa nuts	773,391	711,918	649,635	1,112,108	1,050,613	1,239,673	1,183,561	1,244,832
Cocoa nuts desiccated	2,314,708	2,870,549	3,104,689	4,299,303	4,406,924	5,635,009	7,245,620	6,689,235
Coir fibre	700,603	778,174	793,134	1,049,434	1,240,421	1,586,509	1,856,819	1,745,920
Coir manufactured	10,561	11,559	9,575	3,500	3,586	1,865	2,278	1,445
Coir rope	137,462	165,560	207,670	179,090	215,030	123,872	188,445	201,630
Coir yarn	854,538	799,785	945,357	1,141,647	1,123,077	1,112,551	1,136,232	1,099,586
Copra	4,540,693	4,098,947	7,531,540	8,355,583	10,007,696	12,697,725	15,038,563	10,182,629
Cocoa nut oil	7,601,233	10,007,860	11,022,596	11,984,872	13,141,508	15,634,267	15,142,265	10,586,876
Cocoa nut shells	27,060	32,623	51,993	34,298	26,135	34,020	38,138	15,672
Poonac (oil cake)	937,474	1,283,264	1,499,820	1,215,681	1,038,163	1,307,723	1,137,641	760,418

Exports of Cocoa Nut Palm Products from Ceylon (Quantities)

	1904.	1905.	1906.	1908.	1909.	1910.	1911.	1912.	1913.
Cocoa nut oil (cwts.)	499,632	594,821	539,070	644,348	599,795	619,680	581,277	401,779	545,750
Copra (cwts.)	714,295	393,309	451,134	748,739	784,522	758,711	916,209	614,089	1,154,121
Cocoa nut desiccated (lbs.)	18,728,915	20,779,236	20,213,570	246,452	230,791	242,286	301,134	278,806	34,334,759
Poonac (cwts.)	245,789	270,703	259,125	303,781	254,589	314,777	271,579	173,410	239,968
Cocoa nuts (number)	16,957,621	18,047,718	16,013,510	21,023,853	18,405,186	16,506,491	15,869,613	16,010,809	16,858,007
Coir rope (cwts.)	21,832	21,468	20,643	17,909	21,503	20,309	18,844	20,163	...
Coir yarn (cwts.)	90,722	113,063	102,993	110,732	110,976	110,176	112,721	109,086	...
Coir fibre (cwts.)	126,793	150,920	164,928	173,174	150,354	178,675	195,867	238,840	...

A further classification of the quantities of cocoa nut oil shipped from Ceylon during recent years is given in the following table :—

Shipments of Ceylon Oil

Country.	1904.	1905.	1906.	1908.	1909.	1910.	1911.	1912.	1913.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
England	10,491	15,992	9,313	16,357	14,982	15,083	16,640	8,379	…
America	5,073	5,587	4,896	7,774	9,847	7,508	9,442	8,302	…
Other countries	5,473	8,162	12,744	8,086	5,160	8,393	2,982	3,407	…
Total	21,037	29,741	26,953	32,217	29,989	30,984	29,064	20,088	27,237

(3) *Copra* oil is prepared in modern factories in Europe, the United States, and in Australia [1] from copra (*i.e.* the dried kernels), which is imported in enormous quantities into these countries. The conversion of the kernel into " copra " is not only a convenient method for reducing the cost of freight, but is pre-eminently a cheap process for preserving the cocoa nut oil as far as possible. The earliest process of manufacturing copra consists, as has been pointed out above, in exposing the broken kernel in smaller or larger pieces to the sun, when most of the moisture evaporates. Fully ripe nuts only should be used in the preparation of copra. Copra so prepared is sold as " sun-dried " copra. The sun-dried copra is of much better quality than the kiln-dried (see below), for it gives a light-coloured cocoa nut oil having only a slight yellow tinge, which can be readily removed by treating the oil with char in the course of refining. A more rapid process of obtaining copra is to dry it in kilns by the aid of fire. The primitive method in which these kilns (originally nothing else but grills consisting of a bamboo grating on which the split nuts were placed face downwards) were erected and managed, gave the fumes ready access to the copra itself, so that even the best kiln-dried copra was characterised by a peculiar empyreumatic smell. The inferior brands of copra were partly roasted or even burnt at the outside. Such copra gives a yellowish oil which proves refractory in the bleaching process. At present improved methods of drying copra in kilns are being introduced. In India, as also in some of the Pacific Islands, drying by hot air is being resorted to. The best practice is to bring the nuts, immediately after they have been picked up, into sheds, so as to protect the kernels against the influences of sun or rain, as the case may be. Then the fibres (" coir ")[2] are removed,[3] the nuts split open, when the " milk " runs out, the kernels cut into large pieces, and the " meats " placed on hurdles, consisting of bamboo sticks and cocoa nut leaves arranged on small waggons, which are drawn slowly through a heated tunnel in which the copra is meeting hot air on the counter current principle. The copra prepared by this process is, up till now, chiefly used in confectionery, and fetches a higher price than sun-dried copra.[4]

In the British West Indies drying by means of hot air in a rotary dryer has been introduced, and the results are considered very satisfactory, as thereby the best copra on the market is obtained. Similar plant is being introduced in the Samoa Islands.

It would appear that drying in vacuo would be a still more preferable method.[5] Although *H. S. Walker*,[6] who has carried out experiments on a small scale with a vacuum apparatus, states that this method does not yield satisfactory results, no definite conclusion should be

[1] The northern coasts are now being planted with cocoa nut palms.

[2] Attempts are being made in the Straits Settlements to use this for the manufacture of paper.

[3] For the utilisation of the coir, cp. Gaebelé, English patent 12,596, 1906, and also Société Commerciale des Crins, French patent 421,381.

[4] Detailed instructions as to the erection of a copra drying house are given by A. Dommes, *Der Tropenpflanzer*, 1910, 288.

[5] Bridge, English patent 5633, 1912.

[6] *The Philippine Journ. of Science*, vol. i. p. 118.

drawn from these experiments, inasmuch as they were carried out on too small a scale, and the kernels were exposed for too long a time to an elevated temperature. In the author's opinion a process which combines the rotary dryer with the application of vacuum should yield satisfactory results.[1]

To obtain a perfectly white copra, the fleshy part of the nut must be brought as soon as possible into a drying chamber and heated to a temperature of from 60 to 70° C. Fresh copra yields from 60 to 65 per cent of dry copra.[2]

Whereas the fresh kernels contain about 30-40 per cent of fat, the sun-dried copra contains as much as 50 per cent. In kiln-dried copra the percentage of fat rises to 63 per cent and even 65 per cent. In hot-air-dried copra the percentage of fat reaches even 74 per cent. If the copra is properly dried so that the percentage of water falls to about 4 per cent, fungi do not develop on it, and the fat will consequently undergo little change during transport (in bags) on board ship. A process by which the copra is treated with a mixture of sulphurous anhydride and air has been protected by *Marot*.[3] Copra as now made retains, however, mostly 9 or 10 per cent of water, a proportion which favours the growth of fungi. Hence such copra is easily attacked by them, with the consequent deterioration of the oil (see Vol. I. Chap. I.), and the formation of free fatty acids.

The following table, due to *Schindler and Waschata*,[4] shows in detail the percentages of fat obtained in the examination of some kiln-riedd and hot-air-dried copras :—

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[1] Cp. Lewkowitsch, Evaporation in Vacuo, *Journ. Soc. Chem. Ind.*, 1905, 49.

[2] A. Dommes, *Der Tropenpflanzer*, 1910, 288.

[3] English patent 6379, 1906.

[4] *Chem. Recue*, 1905, 169.

No.	Origin.	Year.	Water.	Fat.
1	Ceylon	1900	...	71·40
2	,, . . .	1900	...	67·86
3	,, . . .	1901	3·65	69·17
4	Penang	1900	..	68·95
5	,, . . .	1900	...	67·08
6	Sangir	1900	...	68·93
7	Malabar . . .	1900	...	71·03
8	Singapore . . .	1900	...	69·05
9	,, . . .	1900	...	65·91
10	Java	1900	...	68 77
11	,, . . .	1900	...	67·06
12	,, . . .	1902	.	66·21
13	Pontianak . .	1900	...	65·43
14	Manila . . .	1900	4·61	64·47
15	,, (special quality)	1900	.	67·55
16	,, ...	1901	.	67·10
17	,, . . .	1901	.	68·57
18	,, . . .	1902	...	68·34
19	Pacific Islands . .	1900	4·10	74·72
20	Zanzibar . . .	1901	...	70 23
21	Tangiers . . .	1903	...	67·00

Means of twenty-one analyses	.	.	.	68·30
Maximum . .	.	.	.	74·72
Minimum . . .	.	.	.	64·47

A comparative examination of the nuts from Zanzibar and Kilosa was undertaken by *Lommel.*[1] The nuts were dried in the shell and the copra pressed. The pressure residues were extracted with carbon tetrachloride. The results are tabulated below :—

	Nuts from Zanzibar.	Nuts from Kilosa.
Yield of copra, per cent . . .	24·30	18·31
Cold pressed oil, per cent . . .	27·38	37·44
Extracted oil, per cent . . .	22·33	16·26

In the following table an attempt is made to classify the different copras on the market in the order of their quality, commencing with the best. It should, however, be noted that the order is subject to great fluctuations, and must vary from year to year :—

Kind of Copra.				Mode of Drying.
Malabar .	.	.	.	Sun-dried
Seychelles [2]	.	.	.	,,
Venezuela (Caracas, Porto Cabello) .	.	.	,,
Ceylon .	.	.	.	,,

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[1] *Pflanzer*, 1910, 119.   [2] Cp. *Bull. Imp. Inst.*, 1909, 394.

Kind of Copra.					Mode of Drying.
Java					Sun-dried
Cébu (Philippines) .		.	.	.	,,
Mozambique . .		.	.	.	,,
Nouméa (New Caledonia)		.	.	.	,,
Dahomey (Quittah) .		.	.	.	,,
Celebes . . .		.	.	.	,,
Borneo . . .		.	.	.	,,
Sumatra . . .		.	.	.	,,
Macassar . . .		.	.	.	Kiln-dried
Manila . . .		.	.	.	,,
Zanzibar . . .		.	.	.	Sun-dried
Saigon . . .		.	.	.	,,
Pacific Islands . .		.	.	.	,,

The copra is treated in the oil mills in a similar manner to that in which palm kernels (see p. 614) are worked up. The meal is expressed twice at a temperature of 55 to 60° C.; the practical yield of oil varies from 63 to 66 per cent according to the content of oil in the raw material. The expressed oil contains, according to the quality of the copra, more or less of free fatty acids.

The author found in a large number of copra oils up to 25 per cent of free fatty acids (see p. 619, "Palm Kernel Oil," and Chap. XIII.).

The oils high in content of free fatty acids are sold for soap-making purposes after a preliminary boiling up with water and filtration. Only the most carefully prepared copra will yield an oil that can be used for edible purposes (cp. Chap. XV. "Vegetable Butters").

According to *Richardson* cocoa nut oils have come on the market having iodine values of 18-24. These oils, he found, had been prepared from copra containing large quantities of rind parings. He shows by experiment that the oils from the "meat" and the rind had the iodine values 8·9 and 40·25 respectively.

The cocoa nut cakes contain from 7 to 10 per cent of fat, but are low in percentage of proteins (about 20 per cent) as compared, *e.g.* with sesamé cakes. Nevertheless the cocoa nut cakes form a valuable food for dairy cattle; they are said to increase the well-being of milch cows and to stimulate the secretion of milk.[1]

It should, however, be stated that *Einecke*[2] demonstrated by experiments that cocoa nut cake has rather a depressing than a stimulating action as regards the quantity of fat in the milk, and that therefore the influence of cocoa nut cake on milk-fat production should be judged as being *nil*. In Germany the press cakes, after extraction with volatile solvents, are used as cattle food.

Trials have been made to extract the cocoa nut oil from copra by solvents, but all attempts have been abandoned owing to the unremunerativeness of the process (cp. Chap. XIII. p. 27). Only under exceptional market conditions, such as the extremely high prices

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[1] Cp. Garola, *Contribution à l'étude des tourteaux alimentaires*, Chartres, 1892; cf. also Collin and Perrot, *Les Résidus industriels utilisés par l'agriculture comme aliments et comme engrais*, Paris, 1904.

[2] *Mitt. des landw. Instit. d. Univ.*, Breslau, 1903, 2,559.

ruling in 1907 for cocoa nut oil, does it pay to extract the oil from the cake by means of solvents, and to sell the residue for manuring the land.

Copra yielding cakes unfit for cattle food is extracted with petroleum ether carbon bisulphide in order to recover the valuable fat.

The amounts of copra coming into the world's markets may be gathered from the following table :—

Exports of Copra

From	1904.	1905.	1906.	1907.	1908.	1909.	1910.	1911.	1912.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
Java		107,709	49,160	68,000	95,000	72,000	104,300	99,700	89,048
Straits (Singapore, Penang)		58,915	36,255	58,914	80,337	74,192	102,946	97,254	81,709
Manila (Philippines)[1]		52,520	57,135	50,694	70,208	77,699	118,200	136,118	...
Tongan Islands[2]		7,582	8,694	7,360	9,886	14,834	12,998	12,721	11,120
Macassar		25,961	9,041	17,290	20,321	19,164	31,168	39,979	...
Sangar		19,514							
Ceylon	31,768	17,739	20,697	19,216	37,436	39,226	34,750	33,637	29,942
Zanzibar	9,211	10,000	7,873	7,158	10,101	7,873	11,279	11,319	9,332
Mozambique		2,514	3,613	2,788	2,650	3,665	3,862	3,411	...
Federated Malay States					4,318	6,268	7,546	8,103	7,771
German New Guinea						8,653	9,243	9,553	11,130

[1] According to a note (Oil and Colour Trades, 1911, 230) the Philippine Islands are the largest producers of copra in the world, and grow about one-third of the world's supply.

[2] Samoa sends to the Australian market alone about 4000 tons per annum. The total production in 1909 was 9214 tons and in 1910, 9124 tons, of which nearly two-thirds is supplied by the natives, whereas the remainder is expressed in the plantations of the Deutsche Handels- und Plantagen Gesellschaft. About 5000 tons were sun-dried, the remainder hot-air-dried copra. The Carolines and the Palau and Marianen Islands produce over 2000 per annum, and the Marshall Islands over 3200 tons per annum.

From the numbers given, the great variation in the production will become at once apparent. (The shortage in the production of 1906 found its commercial expression in the very high prices of cocoa nut oil during 1907.) Almost the total quantity of Ceylon copra went to Germany, France, Austria, and Belgium. The average annual production of copra in the Society Islands is about 6399 tons.

In view of the importance which Marseilles has gained as a centre of the cocoa nut oil industry, the following tables will be found useful :—

Imports into Marseilles of Copra and Cocoa Nut Oil

Year.	Copra.	Cocoa Nut Oil.
	Kilogrammes.	Kilogrammes.
1846	1,370,000	...
1857	960,000	..
1875	712,000	1,076,560
1880	852,900	4,282,895
1885	22,092,943	2,435,402
1890	34,163,594	437
1895	70,957,593	18,211
1900	94,360,000	10,679
1905		1,233,308
1910	146,564,000	738,000
1911	185,108,000	1,011,000
1912	158,935,000	2,189,000

Exports from Marseilles of Cocoa Nut Oil (or Copra [1]) :—

Year.						Tons.
1870	.	.	.	.	.	40
1875	.	.	.	.	.	106
1880	.	.	.	.	.	922
1885	.	.	.	.	.	2,303
1890	.	.	.	.	.	9,437
1895	.	.	.	.	.	7,610
1900	.	.	.	.	.	10,234
1905	.	.	.	.	.	10,776
1910	.	.	.	.	.	43,273
1911	.	.	.	.	.	45,280
1912	.	.	.	.	.	9,520

The quantities of copra imported into France, Marseilles, and Hamburg are placed side by side in the following table :—

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[1] The exported copra is chiefly shipped to the United States.

Year.	France.	Marseilles.	Hamburg.
1896	81,378	75,206	21,084
1897	68,074	63,032	10,791
1898	69,453	63,398	14,096
1899	83,069	74,094	11,523
1900	106,101	94,360	21,034
1901	81,069	74,626	19,983
1902	91,953	85,382	43,522
1903	104,316	95,459	48,652
1904	88,111	81,126	48,586
1905	110,578	102,975	88,165
1906	102,984	97,720	79,942
1907	97,277	94,292	
1908	152,104	162,109	83,669
1909	131,055	133,706	112,159
1910	153,817	146,564	155,989
1911	178,671	185,108	148,066

The following table gives a synopsis of the cocoa nut oil trade of the United Kingdom. The figures given above for the shipments of cocoa nut oil from Ceylon are, of course, included :—

Imports of Cocoa Nut Oil into, Exports from, the United Kingdom, and Home Consumption

Year.	Imports of Cocoa Nut Oil.	Exports of Cocoa Nut Oil.	Sold for Home Consumption.
	Tons.	Tons.	Tons.
1897	12,137	3,568	8,569
1898	15,355	3,350	12,005
1899	22,915	5,299	17,616
1900	27,637	7,040	20 597
1901	23,908	8,138	15,770
1902	24,793	7,334	17,459
1903	39,132	11,075	28,057
1904	30,762	11,330	19,432
1905	30,658	12,860	17,798
1906	26,902	9,152	17,750
1907	23,835	8,199	15,636
1908	37,920	12,141	25,779
1909	33,979	14,958	19,021
1910	51,995	21,166	30,829
1911	56,742	8,704	48,038

Imports and exports of cocoa nut oil of Germany for 1911 and 1912 are given below :—

Imports.			Exports.		
From	1911.	1912.	To	1911.	1912.
	Metric Tons.	Metric Tons.		Metric Tons.	Metric Tons.
Belgium . . .	530	150	France . . .	147	286
India . . .	624	136	United Kingdom .	4102	14,655
			Holland	1541	167
			Austria-Hungary .	1007	1,419
			Sweden . . .	431	444
			Switzerland . .	411	497
			United States of America . .	372	373

Cocoa nut oil is, in our climate, at the ordinary temperature a solid white fat. It has a bland taste, and, in its fresh state, the peculiar though not unpleasant odour of cocoa nuts. The opinion generally accepted up to a short time ago that cocoa nut oil easily turns rancid must be now considered as erroneous. This opinion was due to the fact that the cocoa nut oils imported, as also the cocoa nut oil made from the copra as shipped up to a few years ago, generally contained not only free fatty acids but also products of rancidity (following in the wake of the formation of free fatty acids), which imparted to the cocoa nut oil its peculiar objectionable taste. Even after the free fatty acids were removed, some impurities [no doubt secondary products, formed by the action of fungi (cp. Chap. I.), or enzymes on the putrescible matter of the kernels] still remained in the fat, causing it to become more or less hydrolysed and subsequently rancid on keeping. If the oil is prepared from fresh kernels by boiling (as is done on the Malabar coast and to some extent in Ceylon), or even if the oil is prepared from carefully selected and well-dried copra, the fat undergoes very little change, and only shows a slight proportion of free fatty acids. Those objectionable products of rancidity, which cannot be removed by any practical process of refining, do not appear in a carefully prepared oil. It is, therefore, possible at present to prepare edible cocoa nut oil which behaves as regards keeping quality like any other oil or fat. The best edible cocoa nut oils on the market represent a practically neutral cocoa nut oil (cp. Chap. XV. "Vegetable Butters").

In the preparation of the best brands of vegetable butters the free fatty acids and malodourous substances are removed. *Haller and Lassieur*[1] isolated a small quantity of an essential oil in which they detected methylheptylketone and methylnonylketone. This oil is very difficult to remove. In a further communication these observers describe the isolation of methylheptylketone, methylnonylketone, methylundecylketone, and also d-methylheptylcarbinol and d-methylnonylcarbinol, of which the lævo-isomerides are contained in the oil of rue. An undetermined aldehyde was also detected. They attribute the presence

[1] *Compt. rend.*, 1910, 1013.

of these bodies and the corresponding unpleasant smell of rancid cocoa nut oil ·to the action of a zymase, or enzyme on the copra. Some makers also take out a portion of the liquid glycerides by expression in hydraulic presses. In the manufacture of "cocoa nut stearine" the removal of the liquid glycerides ("cocoa nut oleine") is carried so far that 50 to 80 per cent are expressed, according to the desired melting-point of tho solid product. For the latter the author has proposed the name "Chocolate fat" (cp. Chap. XVI.). In the same manner a technical "cocoa nut stearine" is prepared (from copra oils of ordinary quality) which is used in the manufacture of composite candles and night-lights (cp. Chap. XVI.). The "cocoa nut oleino" is worked up for soap.

The following numbers have been ascertained in the author's laboratory by *Clapham, Calderwood,* and by the author for commercially prepared samples of cocoa nut oleine, cocoa nut stearine (chocolate fats) :—

[TABLE

Fat[1]

Cocoa Nut	Specific Gravity			Saponification Value		Iodine Value		Reichert-Meissl Value	
	At °C.	°	Observer	Mgrms. KOH	Observer	Per cent.	Observer	c.c. norm. KOH	Observer
"Oleine"	60	0·92931	Clapham	265·35	Calderwood	14·8	Calderwood	7·95	Calderwood
"Stearine"[4]				255·63	Lewkowitsch	4·0	Lewkowitsch	4·45	Lewkowitsch
				251·5	"	5·2	"	3·85	"
								6·34	"
				254·3	"	6·64	"	3·24-4·89	"
				257·4	"			5·88	"

Fatty Acids

Cocoa Nut	Insoluble Acids + Unsaponifiable		Titer Test		Neutralisation Value		Mean Molecular Weight		Iodine Value	
	Per cent.	Observer	°C.	Observer	Mgrms. KOH	Observer		Observer	Liquid Fatty Acids	Observer
"Oleine"	85·25	Clapham	20·6[2]	Calderwood	267	Clapham	210·0	Clapham	36·3	Clapham
"Stearine"			20·1[3]	"	266·9	"	210·2	"		
			20·6	Clapham			204·6	Calderwood		
			26·55[2]	Calderwood			211·4	"		
			26·12[3]	"						

[1] Determined in the author's laboratory. [2] Fatty acids washed with water. [3] Fatty acids washed, with brine

[4] Cp. also Chocolate Fats.

The quantity of edible cocoa nut oil (including edible palm kernel oil) produced a few years ago in Europe alone, amounted to about 10,000 tons per annum,[1] and rose rapidly to 50,000 tons. The remunerativeness of this manufacture led to an over-production and the flooding of the market with inferior qualities (cp. Chap. XV. ' Vegetable Butter ").

Neutral cocoa nut oil dissolves completely in two volumes of absolute alcohol at 32° C. (*Milliau*[2]). One volume of cocoa nut oil dissolves also in two volumes of 90 per cent alcohol at 60° C. (cp. also Vol. I. 368). As to the characteristic crystalline form of cocoa nut oil crystals under the microscope see " Butter Fat."

Cocoa nut oil resembles palm kernel oil in its chemical composition ; like the latter it contains large proportions of trimyristin and trilaurin, smaller quantities of tripalmitin,[3] tristearin, and triolein, as also the glycerides of the volatile acids caproic, caprylic, and capric. It is practically free from hydroxy acids [4] (*Lewkowitsch*), and free from butyric acid.

The occurrence of tristearin in recorded here, as a specimen of commercial cocoa nut oil examined in the author's laboratory yielded 0·99 per cent of stearic acid.

Ulzer [5] doubted the occurrence of palmitin in cocoa nut oil, as he could not detect any palmitic acid. In view of the fact that *Oudemans* did identify palmitic acid, and of the further fact that the presence of stearic acid had been proved by the author, this statement stood in need of confirmation. *J. J. Reijst* [6] lately averred that stearin did not occur in cocoa nut oil. The statements of *Ulzer* and *Reijst* have recently been shown to be erroneous by *Haller and Youssoufian*,[7] who have proved, in an exhaustive examination of the fatty acids obtained by fractionation of the methylesters (Chap. XII.), that both palmitin [8] and stearin occur in cocoa nut oil. These chemists confirm the occurrence of caproic, caprylic, capric, lauric, myristic, palmitic, stearic, and oleic acids, all of which have been identified by their methylesters. They could not detect butyric acid, the absence of which from cocoa nut oil had already been recognised by *A. Kirschner* and by *O. Jensen* (cp. below).

By treatment with hydrogen in the presence of a catalyst until the percentage of oleic acid had fallen from 13 to 1, the melting point had risen from 25·6 to 44·5° C., whereas the solidifying point had only risen from 20·4° to 27·7° C.

Tolman and Munson obtained, by the lead-salt-ether method, 65·9 per cent of solid acids ; this agrees with a later statement of *Lane*,[9] who

[1] Lewkowitsch, *Cantor Lectures on Oils and Fats, their Uses and Applications*, 1904, p. 22.
[2] *Compt. rend.*, 1892 (115), 517.
[3] Oudemans, *Journ. f. prakt. Chem.*, 1860 (81), 375.
[4] Unpublished experiments. [5] *Chem. Revue*, 1899, 203.
[6] *Rec. des trav. des chim. des Pays-bas*, 1906, xxv. 271.
[7] *Compt. rend.*, 1906 (143), 803.
[8] Confirmed also by K. S. Caldwell and by W. H. Hurtley, *Proc. Chem. Soc* 1909, 73.
[9] *Journ. Soc. Chem. Ind.*, 1904, 1104.

obtained from cocoa nut oil, by treating the lead salts with both cold and hot ether, 34·5 and 37·5 per cent of liquid fatty acids respectively. Of course the liquid acids must not be taken in this case to represent oleic acid, as the iodine value of cocoa nut oil does not allow for so high a percentage of this unsaturated acid. Indeed, the proportions of the liquid acids were found by *Lane* to amount to 22·17 and 19·52 per cent respectively. It is evident that lead salts of the volatile acids had passed into the ethereal solution.

The amount of total volatile fatty acids found in the author's laboratory in the examination of a number of cocoa nut oils has been given above (Chap. VIII.). Tested by *Polenske's* method (see below) the author obtained, with a number of edible cocoa nut oils, the *Reichert-Meissl* values (*i.e.* soluble volatile acids by *Reichert-Meissl's* method) 7·3-7·5, whereas the insoluble volatile acids (for 5 grms.) required from 15·5-20·5 c.o. of decinormal alkali. (The numbers which *Polenske* gives for the latter, viz. 16·8-17·8, having been derived from too small a number of observations must, therefore, be corrected.) *Muntz and Coudon* found in four edible cocoa nut oils from 2·26 per cent to 2·70 per cent of total volatile acids calculated to butyric acid (as determined by the French official method, see Vol. I. Chap. VIII.), and from 8·89 per cent to 10·06 per cent of total insoluble volatile acids (also expressed in terms of butyric acid). Since the highest and lowest values for the soluble volatile and insoluble volatile acids are not in strict correspondence, the figures are given in detail in the following table :—

Edible Cocoa Nut Oil.	Soluble Volatile Acids in terms of Butyric Acid.[1]	Insoluble Volatile Acids in terms of Butyric Acid.[1]
No.	Per cent.	Per cent.
1	2·51	9·63
2	2·49	10·06
3	2·26	9·76
4	2·70	8·89

The same edible cocoa nut oils, examined by *Muntz and Coudon's* method (see below), gave the following figures :—

Edible Cocoa Nut Oil.	Soluble Volatile Acids in terms of Butyric Acid.	Insoluble Volatile Acids in terms of Butyric Acid.	Relation :— $\dfrac{\text{Insol. Vol. Acids}}{\text{Sol. Vol. Acids}} \times 100.$
No.	Per cent	Per cent.	
1	1·20	3·01	250·3
2	1·23	3·38	274·4
3	1·15	3·63	314·7
4	1·27	3·60	282·3

It should, of course, be noticed that these numbers refer only to the

[1] It should be remembered that cocoa nut oil contains no butyric acid.

special brands of edible cocoa nut oil examined, and do not apply generally to all kinds of cocoa nut oil.

Segin, who attempted to determine separately the molecular weights of the total volatile acids, of the soluble volatile acids, and of the insoluble volatile acids, found the following numbers respectively :—114, 163, 156. These figures agree, as regards the insoluble volatile acids, with a figure which the author has derived as the mean of a number of experiments, viz. 161. *Kirschner* could not detect butyric acid amongst the volatile acids of cocoa nut oil ; he found that caproic acid is only present in small quantities, and that the bulk of these fatty acids consists of caprylic acid. *O. Jensen* confirms the absence of butyric acid, and gives as the numbers of decinormal KOH required for the neutralisation of the volatile acids from 5 grms. of a specimen of cocoa nut oil (of the acid value 0, *Reichert-Meissl* value 6·8, and insoluble volatile acid number 13·0 by *Polenske's* method), the following amounts of alkali, for caproic acid 21·4 c.c., caprylic acid 20·5 c.c., capric 31·2 c.c. It will be seen that the statements of the two observers do not agree.

Paulmyer [1] resolved the fatty acids of cocoa nut oil by fractional distillation in a current of steam, into ten equal fractions. The neutralisation values and mean molecular weights of the several fractions were determined with the following result :—

	Neutralisation Value.	Molecular Weight	Corresponding to		
			0·25 per cent Caproic Acid,		$C_6H_{12}O_2$
1st Fraction	329·1	170	0·25 ,, Caprylic ,,		$C_8H_{16}O_2$
			9·50 ,, Capric .,		$C_{10}H_{20}O_2$
2nd ,.	310·8	180 }	10 ,, Capric ,,		$C_{10}H_{20}O_2$
3rd .	292·8	191 }			
4th ,,	281·6	199 }	20 ,, Lauric ,,		$C_{12}H_{24}O_2$
5th ,,	276·0	203 }	20 ,, Lauric ,,		$C_{12}H_{24}O_2$
6th ,,	268·2	209 }			
7th ,,	261·4	214 }	10 ,, Myristic .,		$C_{14}H_{28}O_2$
8th ,,	245·7	228	10 ,, Myristic ,,		$C_{14}H_{28}O_2$
9th ,,	230·0	244	4 ,, Myristic ,,		$C_{14}H_{28}O_2$
			6 ,, Palmitic ,,		$C_{16}H_{32}O_2$
			4·6 ., Palmitic ,,		$C_{16}H_{32}O_2$
10th ,,	207·6	270	5·4 ,, Oleic .,		$C_{18}H_{34}O_2$

According to this examination the total fatty acids of cocoa nut oil would seem to consist of—

0·25	per cent	caproic	acid.
0·25	,,	caprylic	,,
19·50	,,	capric	,,
40·0	,,	lauric	,,
24·0	,,	myristic	,,
10·6	.,	palmitic	,,
5·4	,,	oleic	,,

[1] *La Savonnerie marseillaise,* 1907, No. 78.

It should, however, be borne in mind that notable quantities of caproic and caprylic acids must have been lost, and that the proportion of these two acids must be somewhat higher. It would further appear that the amount of oleic acid is too low.

An investigation carried out by *Elsdon*, who fractionated the methyl-esters prepared by *Haller's* method (Vol. I. p. 665), led to the following composition :—

	Per cent.
Caproic acid	2
Caprylic acid .	9
Capric acid	10
Lauric acid .	45
Myristic acid .	20
Palmitic acid	7
Stearic acid	5
Oleic acid	2
	100

Here again the amount of oleic acid appears to be too low, and the stearic acid much too high.

The proportion of unsaponifiable matter in cocoa nut oil is small. The author obtained from a large number of cocoa nut oils amounts of unsaponifiable matter, varying from 0·179 per cent to 0·297 per cent.[1] The phytosteryl acetate prepared from the unsaponifiable matter melted at 129·5° C. *Siegfeld*[2] found in an edible cocoa nut oil 0·17 per cent of unsaponifiable matter, from which he prepared a phytosterol which melted, after the sixth crystallisation, at 140·8° to 141·8° C. The melting point of the acetate, after the seventh crystallisation, was 128·3°-129·3° C. From another specimen of cocoa nut oil *Siegfeld* obtained 0·184 per cent of unsaponifiable matter, from which he isolated a phytosterol which melted, after the seventh crystallisation, at 140·7°-141·7° C. The melting point of the acetate after the seventh crystallisation was 129°-130° C.

Konig and Schluckebier[3] found in the fat extracted from cocoa nut *cake* 0·56 per cent of unsaponifiable matter, which consisted almost entirely of phytosterol, melting at 137° C.

H. Matthes and E. Ackermann[4] state (in a preliminary communication) that the unsaponifiable matter of a specimen of cocoa nut oil examined by them consisted of 0·125 per cent of crude phytosterol, melting at 135-140° C., and of 0·025 per cent of a liquid substance. The acetylated crude phytosterol melting from 126°-128° C. yielded, on brominating in a solution of ether and glacial acetic acid, thin crystals of a bromide melting from 180° to 183° C. From the filtrate there were obtained after boiling down and recrystallising from alcohol micro-crystalline aggregates, melting at 132-135° C. (the melting point of the di-bromide of phytosterol acetate from purified cotton seed oil phytosterol)

[1] With regard to the proteins in cocoa nut oil, cp. Chap. XV. " Vegetable Butters."
[2] *Zeits. f. Unters d. Nahrgs- u. Genussm.*, 1904, 581.
[3] *Ibid.*, 1908 (xv.), 642.   [4] *Berichte*, 1908, 2000.

Physical and Chemical Characteristics of Cocoa Nut Oil

Specific Gravity			Solidifying Point		Melting Point		Saponification Value		Iodine Value	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15·5	0·9259	Tolman and Munson	19·5-15·7	Valenta	23·5-24·1	Valenta	257·3-268·4	Valenta	8·9	Hubl
18	0·9250	Stillwell	16-14	De Negri and Fabris	26·2-26·4	Filsinger			9·-9·5	Thorner
37·8 (=100° F.)	0·910·	Moore			24-27	De Negri and Fabris			9·10	Lewkowitsch
(water at 37·8=1)	0·9167		20-16	Thorner			253·4-262	De Negri and Fabris	8·54 [1]	Crossley and Le Sueur
			22-23		23-26	"	255-260	Thorner	8·41 [2]	"
					23·5-25	Crossley and Le Sueur	258·2 [1]	Crossley and Le Sueur	8·25 [3]	"
99 (water at 15·5=1)	0·8736	Allen					255·6 [2]	"	8·7·4 [4]	Wijs
100 (water at 100=1)	0·9030 [1]	Crossley and Le Sueur					255·5 [3]	"	8·39 [5]	"
	0·9040 [2]	"					251-261	Lewkowitsch	8·84 [6]	"
	0·9042 [3]	"					225-260 [8]	"	9·32 [7]	"
									8·0	Lane

[1] Malabar oil.   [2] Bengal oil.   [3] Bombay oil.   [4] "Cochin prima."   [5] "Cochin neige."

[6] Ceylon oil   [7] "Ceylon prima."   [8] Edible cocoa nut oil.

Physical and Chemical Characteristics of Cocoa Nut Oil—continued

Reichert Value.		Refractive Index.			Viscosity.	
c.c. n/10 norm KOH	Observer.	At 60° C.	Observer		Seconds at 140° F.	Observer.
3·7	Reichert { Allen	1·411	Thorner		63·9 [1]	Crossley and Le Sueur
3·5-3·7	Moore { Minter				64·7 [2]	,,
		Butyro-refractometer			64·5 [3]	,,

Reichert-Meissl Value.					
c.c. n/10 norm KOH	Observer.	At ° C.	"Degrees "	Observer.	
7·0	Lewkowitsch	15·5	49·1	Tolman and Munson	
7·5	Thorner	40	33·5	Beckurts and Seiler	
6·71 [1]	Crossley and Le Sueur	,,	35·5	Mansfeld	
6·79 [2]	,,	,,	34·2	Crossley and Le Sueur	
6·65 [3]	,,				
8·4 [4]	Ulzer				
8·0	Menon				

[1] Malabar oil.　　[2] Bengal oil.　　[3] Bombay oil.

[4] In view of the figures given by O. Jensen the correctness of this high number is open to doubt.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

| Insoluble Acids + Unsaponifiable | | Specific Gravity | | Solidifying Point | | Melting Point | | Neutralisation Value | | Mean Molecular Weight | | Iodine Value | | Refractive Index | |
Per cent.	Observer	At 98°-99° C. (water at 15·5=1)	Observer	°C	Observer	°C	Observer	Mgrms. KOH	Observer		Observer	Per cent.	Observer	At 60° C.	Observer
88·6-90·5	Lewkowitsch	0·8354	Allen	20·4	Hübl	24·6	Hübl	258	Thörner	196·	Alder	8·39-8·79	Morawski and Demski	1·4295	Thörner
86·25[1]	Clapham			19·5-15·7	Valenta	24·25	Valenta			204	Wright	9·3	Williams		*
				18·16	De Negri and Fabris	25·27	De Negri and Fabris			201	Williams	8·02-8·92	De Negri and Fabris		
				20	Thörner	24·25	Thörner			211[2]	Lewkowitsch	8·5-9	Thörner		
				Titer Test.								_Iodine Value of the Liquid Fatty Acids._			
				21·2-22·55	Lewkowitsch							36·3[1]	Clapham		
				21·9-24·7	"							31·9	Tolman and Munson		
				23·0-23·6	"							22·2	Lane		
				23·3-23·9	"										
				23·25·0	"										
				24·8-25·2 (Cochin)	"										

1 Determined in the author's laboratory in a sample of commercial "cocoa nut oleine" (see p. 640).   2 Ceylon oil.

The " titer test " of the fatty acids of cocoa nut oil varies according to the amount of washing given to the fatty acids in the course of their preparation. Thus a sample of cocoa nut oil, the fatty acids of which were washed as described in Vol. I. Chap. III., had the titer test of 22° C., whereas by washing with brine, in which the volatile fatty acids are less soluble than in water, a titer test of 21° C. was obtained. The respective mean molecular weights, calculated from the neutralisation values 261·4 and 267·7, were in the same order, 214·6 and 209·5.

In the valuation of cocoa nut oil for soap-making, due regard must therefore be paid to the manner in which the fatty acids are prepared for the titer test.

Cocoa nut oil is used in enormous quantities in the manufacture of soaps, made by the boiling process as also by the cold process. It is also used extensively as a vegetable butter and as a chocolate fat (see Vol. III. Chap. XV.). Its use for batching juto after it has been boiled with caustic alkali has been patented.[1]

In the German colonies cocoa nut oil has been proposed as a fuel for driving Diesel motors. Cocoa nut oil is also used in the manufacture of a sulphonated oil similar to Turkey red oil. Its use as a solvent for ozone has also been patented.

Cocoa nut oil is not adulterated with other fats, at any rate this holds good for the oil imported into England. Nevertheless, if the prices are high (as was the case in 1907), the inducement to adulterate cocoa nut oil may present itself. *Milliau* states that cocoa nut oil is being adulterated with sesamé oil, cotton seed oil, etc. The colour reactions which he proposes for their detection are not required, as the usual tests, such as saponification value, iodine value, etc., readily reveal any adulteration that may have been practised. A method for the detection of arachis oil in cocoa nut oil is given by *Muntz Paulmyer and Rivals.*[2] As these methods offer no advantage over the *Renard* test cp. " Arachis Oil," p. 310, the reader must be referred to the original publication. Owing to the great similarity of cocoa nut oil to palm kernel oil, and the other oils of the cocoa nut oil group, the detection of palm kernel oil in cocoa nut oil, and *vice versa*, is a very difficult problem, requiring extended research. Since cocoa nut oil and palm kernel oil have nearly the same price, and since the uses they are put to are practically identical, the examination of cocoa nut oil for admixtures with palm kernel oil, and *vice versa*, is but rarely required. This problem may assume importance in the examination of edible fats with a view to ascertaining their origin, as the properties of palm kernel oil and cocoa nut oil differ somewhat. It should be pointed out that attempts are made to impart to edible cocoa nut oil a more desirable consistence by adding paraffin wax, or heavy paraffin oil. This addition is easily detected by determining the amount of unsaponifiable matter (cp. also " Margarine," Vol. III. Chap. XV.). *Arnold* [3] found recently in an edible cocoa nut oil (or palm kernel oil) 3·9 per cent of unsaponifiable

[1] German patent 184,786.
[2] *Les Corps gras indus.*, 1909, 178.
[3] *Zeits. f. Unters. d. Nahrgs· u. Genussm.*, 1908 (xv.), 280.

matter, which consisted of a viscous, yellow liquid showing in the butyro-refractometer at 40° C. 74·4 " degrees," having the saponification value nil, and the iodine value 2·65. For the detection of cocoa nut oil in butter, cp. " Butter Fat."

In the present state of our knowledge, it is impossible to detect with any degree of accuracy palm kernel oil in admixture with cocoa nut oil. *Burnett and Revis* propose a method based on the temperature at which alcoholic solutions of the barium salts of the insoluble volatile fatty acids become turbid. They state that the turbidity temperatures for cocoa nut and palm kernel oils are 52·5° C. and 68·5° C. respectively.

(*i*) The fat from *Cocos acrocomoides*, Dr., from Brazil was examined by *Niederstadt*.[1] Its iodine value was 4·8 and the saponification value 292·8. The exceedingly high saponification value was probably due to the rancid state of the specimen, as its acid value was 131.

The *Reichert-Meissl* value of the sample was not determined; most likely it would have approximated that of the other fats belonging to the cocoa nut oil group.

(*j*) TONKA BUTTER

This fat is stated to be derived from the tonka bean from *Dipteryx odorata*, Willd., *Coumarouna excelsa*, Aubl., a tree growing in the forests of Guyana. The seeds are the tonka-beans of commerce. The tree belongs to the *Papilionaceæ*, whereas all the preceding fats of the cocoa nut oil group are derived from palms. Nevertheless the fat would also appear to belong to the cocoa nut oil group, on account of its high saponification value in association with a high *Reichert-Meissl* value.

The following characteristics were ascertained by *Duyk*[2] :—

Specific gravity at 100° C.	0·888
Melting point	28° C.
Saponification value	257
Reichert-Meissl value	5·4
Butyro-refractometer, " degrees "	47
Critical temperature of dissolution	32·5° C.

This fat is becoming an article of commercial importance in the West Indies, and is said to be used there for flavouring dietetic articles.

[1] *Berichte d. Deutsch. Pharm. Ges.*, 1902, 144.
[2] *Répert. Pharm.*, 1908, 193.

JAPAN WAX,[1] JAPAN TALLOW

French—*Cire du Japon* ; *suif végétal vert.*   German—*Japanwachs,
Sumachwachs, Japantalg.*   Italian—*Cera giapponesa.*

For table of characteristics see pp. 652, 653.

Japan wax is obtained from the berries of several species of the
sumach tree, viz.—*Rhus* [2] *succedanea*, L., *R. acuminata*, D. C., *R. verni-
cifera*, D. C. (known in Japan as *Urushi-noki*), *R. sylvestris*, Sieb. et
Zucc.   The first three species grow chiefly in China, the last named one
flourishes especially in the western provinces of Japan.   *R. succedanea*
occurs also in Indo-China (Tonkin, North Annam, Cambodja) and in
India (Sikkim, Nepal, Butan, and Kashmir).   In China, Japan, and
Tonkin the trees are grown chiefly for the sake of the lacquer they exude.
The Japan wax is a by-product of the lacquer industry, and is only
prepared in India and China.

The following data, due to *Rein*,[3] show the difference between the
berries of *Rhus succedanea* and *Rhus vernicifera* :—

	Rhus succedanea.	*Rhus vernicifera.*
100 berries weigh . .	8·75 gr.	12·80 gr.
The epidermis forms . .	5·7 per cent	4·7 per cent
The mesocarp ,, .	39·3 ,,	42·4 ,,
The endocarp ,, . .	55·0 ,,	52·9 ,,
Japan tallow (by extraction with ether)	24·2 ,,	27·0 ,,

The seed consists of a small kernel surrounded by a greenish,
striated, shrivelled mass.   In China the fatty matter is prepared in
the same manner as *mou-iéou* (see "Vegetable Tallow of China," p. 592).
From 48 kilos. of seed 5·7 kilos. of the wax (known in China under
the name *Tsi-la*, *i.e.* wax of Tsi) are obtained.

The manufacture of Japan wax is carried out in a somewhat crude
fashion, by storing the berries in straw until they have fully matured,
then crushing them by hand in a wooden, funnel-shaped trough, and
winnowing them so as to separate the kernels.   The powdered mass
thus obtained is put into hempen sacks, and then subjected to pressure
in wooden wedge presses.

With the growing demand for Japan wax the aim has been to increase
the output ; this is accomplished by mixing the press residue, or even
the ground berries, with a certain proportion (usually 10 per cent) of
the kernel oil, haze-kernel oil (*hazé* is the Japanese term for *Rhus suc-
cedanea*).[4]   This practice has been on the increase during the last few

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[1] Not to be confounded with Japanese beeswax.
[2] The oil from *Rhus glabra* has been described above, table facing p. 404.
[3] *Industries of Japan*, 1889, p. 161.
[4] Private communication from Tsujimoto.

years; therefore the discrepancies in the iodine values recorded in the table of characteristics are readily explained. The samples analysed by *Hübl* and by *Lewkowitsch* date back some decades. Those commercial samples which have higher iodine values undoubtedly contained some kernel oil. Since perilla oil has a very high iodine value, it is evident that a small quantity only is required to raise the iodine value of a commercial specimen.

The berries yield from 15 to 25 per cent of a coarse, greenish, tallow-like mass. This is refined by remelting, pressing through cotton sacks, and allowing the fat to drop into cold water. The thin flakes of wax are then bleached by exposure to the sun in shallow baskets (in a similar manner as is done in the process of bleaching beeswax), the material being frequently turned over, and sprinkled with water. Finally the wax is melted and cast into slabs. In this form (termed in Japan *Ki-yu*) it is exported to Europe.[1]

The chief market for Japan wax is Kobe. In this town and in Osaka the three most important refineries are situated. It is stated that an average harvest yields about 2400 tons of crude wax. Older statistics, of the years 1900, 1901, 1902 give the quantities of Japan wax exported as 222, 240, 252 tons respectively. According to the latest statistical data of the Japanese Government the following quantities were exported in the years 1905, 1906, and 1912 :—

Year.	Total.		Exports to				
	Quantity. Kin.	Value Yen.	Hongkong Kin.	England. Kin	Germany Kin.	America. Kin	Manila. Kin.
1905	3,158,188	804,299	838,430	365,301	471,970	691,555	56,343
1906	3,913,626	1,092,447	917,651	496,692	797,141	812,218	118,667
1912	5,238,627	1,142,623	327,121	986,484	990,137	1,532,596	95,333

(1 kin = 600 grms. ; 1 yen = 2s. 0½d.)

It is hardly to be expected that the production of Japan wax can be largely extended, for it takes seven to eight years for the wax tree to reach maturity, and if the tree promises to be a fruitful source of lacquer, this leads to its sacrifice as a source of wax.

The exported Japan wax is a pale yellow, hard substance, of conchoidal, somewhat lustrous fracture. It has a wax-like consistence, and can be easily kneaded between the fingers. Its odour recalls that of tallow and beeswax.

On keeping, Japan wax turns deep yellow, and becomes coated with a white powder consisting of microscopical prismatic needles. Under the microscope Japan wax exhibits a crystalline structure.

[1] In Europe it is sometimes termed "*Tertia*" (cp. "Prima" and "Secunda" "Vegetable Tallow of China").

Physical and Chemical Characteristics of Japan Wax

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value		Iodine Value.	
At °C.	Observer.	°C.	Observer.	°C	Observer.	Mgms. KOH	Observer.	Per cent.	Observer.
15	0 975 Dieterich	50·8	Rudorff	50·4-51	Rudorff	220	Hubl	4·2	Hubl
22	0 9692 Eberhardt	48·5	Eberhardt					4 9-6 6	Lewkowitsch
,,	1·002 ,,			(cp. p. 654)		221 6	Henriques	8·3-8·5	Gettel and van der Want
60	0 9018 Allen					217 5-237·5	Gettel and van der Want		
(water 15·5=1)				52·53	Eberhardt			10 6-11 3	Bernheimer and Schiff
98-99 (water 15·5=1)	0 8755 ,,			52 6-53 4	Bernheimer and Schiff	220·3-222·1	Bernheimer and Schiff	13·1-15 1	Ahrens and Hett
Bleached Japan Wax.									
22	0 9749 Eberhardt								

Refractive Index in Butyro-refractometer, observed at 84° C. and calculated to 40° C.:—47 6-49 7; "degrees" (Berg, *Chem. Zeit*, 1903, 755).

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity		Solidifying Point		Melting Point.		Mean Mol. Weight.	
Per cent.	Observer.	At 98°-99° C. (Water 15·5=1.)	Observer	°C.	Observer	C.	Observer		Observer
89·8	Lewkowitsch	0·848	Allen	53·0-56·5	Allen			257·6	Harris[2]
90·62-	Geitel and					59-62	Eberhardt.	262-	Geitel
90·66	van der Want			Titer Test				263	and van der Want
				58·8-59·4	Lewkowitsch	54-56	Parry[1]		

The numbers for the specific gravity recorded in the table vary considerably ; this is no doubt due to the samples having been derived from different sources.

Kleinstück [3] determined the specific gravity of several samples of Japan wax at different temperatures, and states that its density is equal to that of water at 16°-18° C. ; below 16° C. it is heavier, and above 18° C. lighter than water. Japan wax which has been freshly melted has a higher specific gravity than the normal one, the density only becoming normal after keeping for some time. This phenomenon is due to the coefficient of expansion of Japan wax being higher than that of water, as is shown in the following table due to *Kleinstück* :—

Specific Gravity of Japan Wax compared with that of Water

Temperature °C.	Japan Wax.		Water
	Kept for some time.	Freshly melted	
4	..	1·00237	1·00000
6·5	.		0·99995
7·2	1·00737		0·99991
17·0	.	0·99123	0·99884
17·5	0·99846	...	0·99875
23·0		0·98747	0·99762
26·5	0·98615	0·98683	0·99674

[1] Samples, *Chemist and Druggist*, 1905, 34.

[2] Determined in the author's laboratory , the fatty acids had been previously freed from unsaponifiable matter. This specimen of Japan wax contained 1·1 per cent of unsaponifiable matter.

[3] *Journ. Soc. Chem. Ind.*, 1890, 1072.

The melting points recorded in the table vary considerably. *Rouber's* [1] statement that Japan wax has two melting points, inasmuch as a specimen of the normal melting point melted at 42° C. immediately after solidification, is due to the phenomenon described in Chap. I. *Eberhardt* also found that a specimen of the melting point 53° C. melted at 48°-49° C. after rapid cooling.

Japan wax is insoluble in cold alcohol, but dissolves readily in boiling alcohol, separating on cooling almost completely as a granular, crystalline mass. Like all other fats it dissolves easily in ether, benzene, and petroleum ether. The following amounts of unsaponifiable matter were found :—

Unsaponifiable. Per cent.			Observer.
1·14	.	.	. Allen and Thomson
1·1	.	.	. Harris [2]
1·48-1·63	.	.	Geitel and v. der Want
0·68	.	.	. Matthes and Heintz

In a 10 per cent chloroform solution Japan wax proved to be optically inactive.[3]

Japan wax consists chiefly of palmitin and free palmitic acid. Besides these constituents, it also contains small quantities of dibasic acids (see Vol. I. Chap. III.) and of soluble acids.[4] *Geitel and v. der Want* found 4.66-5·96 per cent of soluble acids. Stearic and arachidic acids, previously stated to occur in Japan wax, could not be detected by *Geitel and v. der Want*. On distilling the insoluble Japan wax fatty acids, first under a pressure of 15 mm. up to 250° C., to remove the bulk of palmitic acid, then purifying the residue by crystallising it from 75 per cent alcohol and fractionating the recrystallised product in the vacuum of the cathode light, the remainder of the palmitic acid distils over at 135°-180° C. The higher fractions obtained subsequently were found to consist chiefly of japanic acid, which was accompanied by smaller quantities of its lower homologues, $C_{19}H_{36}O_4$ and $C_{20}H_{36}O_4$. These acids were identified by the composition of the hydrocarbons obtained from them (see Vol. I. Chap. III.). 1000 grms. of Japan wax yielded about 6-7 grms. of mixed dibasic acids.[5] The dibasic acids very likely occur as mixed glycerides (*Geitel*) ; as an example may be given the formula of the mixed glyceride that would be formed by the combination of japanic and palmitic acids with glycerol :—

$$C_{20}H_{40} \diagdown \begin{matrix} \diagup CO.O \\ \diagdown CO.O \diagdown \\ C_{16}H_{31}O.O \diagup \end{matrix} C_3H_5.$$
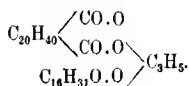
By using *Haller's* method of " methanolysis," *Tassilly* isolated

[1] *Journ. de Pharm.*, 1872 (4), 16, 20.

[2] Determined in the author's laboratory.

[3] *Chem. Zeit.*, 1906, 711.

[4] Engelhardt expressed the opinion that the soluble acids consist in the main of isobutyric acid ; this stands, however, in need of confirmation.

[5] Schaal, *Berichte*, 1907, 4786.

pelargonic acid and an acid of the suggested formula $C_{15}H_{30}O_2$. Traces of stearic and oleic acid were also detected.

An exhaustive examination by *Matthes and Heintz* [1] showed that the unsaponifiable matter contained besides a phytosterol, melting at 139° C. (having $[a]_D = -22.11°$ and absorbing 61·81 per cent of iodine), ceryl alcohol, melissyl (myricyl) alcohol, a saturated alcohol, melting at 65° C. (probably $C_{19}H_{40}O$) a liquid portion, which on fractionation in vacuo gave the results collated in the following table :—

Fraction.	Boiling at 15 mm. pressure. ° C.	Consistence.	Iodine Value.	n_D^{40}	Phytosterol Colour Reaction.
1	100-130	Mobile, colourless oil	23·82	1·4326	Positive
2	130-185	Viscous, almost colourless oil	34·44	1·4461	Positive
3	185-285	Semisolid	..	..	Positive
4	285-300	Viscous, yellowish brown oil	51·81	1·4596	Positive
5	300-315	Viscous, brown oil, partly decomposed	146·4	1·4966	..

Fraction 3 yielded on crystallisation from petroleum ether a crystalline acohol melting at 65° C., which no longer exhibited the phytosterol colour reaction, and gave an acetate melting at 41° C. The acohol is saturated, and yields proportions of carbon and hydrogen corresponding best to the formula, $C_{19}H_{40}O_2$. (The uneven number of carbon atoms would, however, suggest the formula $C_{20}H_{42}O$.) The oily substance which remained dissolved in the petroleum ether solution had iodine value 44·66 and $n_D^{40} = 1·4677$.

The amounts of free fatty acids in commercial samples vary considerably, as is shown in the following table :—

Free Fatty Acids. Per cent.			Observer.	
9·13	.	.	Hubl	
3·87		.	Nördlinger	
8·96	.	.	Allen	
9·03	.		,,	•
12·72	.		,,	
9·40		.	Harris [2]	
10·9·16·4	.	.	Geitel and v. der Want	

Commercial Japan wax contains from 0·02 to 0·08 per cent of ash.

Japan wax is readily distinguished from true waxes by its saponification value, and by its yielding glycerol on saponification ; hence the name Japan tallow would appear to be preferable. Its detection in beeswax will be described under " Beeswax."

Adulteration of Japan wax with other fats is easily detected. The

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[1] *Archiv der Pharm.*, 1909 (247), 650.
[2] Determined in the author's laboratory.

presence of tallow will be indicated by a low melting point and a high iodine absorption of the sample.

Commercial Japan wax is frequently adulterated with from 15 to 30 per cent of water.[1]   La Wall [2] found in a number of commercial samples starch to the extent of 20-25 per cent.   On treating the adulterated wax with a solvent (Vol. I.) the fat only is dissolved.   A rapid method to detect starch qualitatively is to moisten a freshly cut surface with iodine solution.

Japan wax is largely used for waxing floors, and as a constituent of polishes.   Like beeswax and other animal waxes it forms an emulsion with water, and is therefore used for currying leather.[3]   The difficulties which Japan wax fatty acids offer to their application as candle material have not yet been overcome.

MYRTLE WAX, LAUREL WAX, BAYBERRY TALLOW

French—*Cire de Myrica.*   German—*Myrtenwachs, Myricawachs.*
Italian—*Cera mirica.*

For table of characteristics see p. 658.

Myrtle wax is obtained from the berries of various species of *Myrica*. In North America, where the Myrica shrubs are common along the Atlantic sea-coast, the myrtle wax is obtained from *Myrica cerifera*, L., and *Myrica carolinensis*, Willd.   In South America, notably in New Granada and Venezuela, it is obtained from *Myrica arguta*, Kunth, and *Myrica caracassana*, Humb., Bonpl., et K., and in South Africa (Cape Colony [4]) from *M. quercifolia*, L., *M. cordifolia*, L., *M. laciniata*, Willd., and *M. serrata*, Lam.   In Abyssinia myrtle wax is obtained from *M. ethiopica*, L.

The wax from the fruits of the Mexican plant *Myrica jalapensis* ("arbol de la cera"), occurring in dense thickets covering considerable areas in Vera Cruz (from Jalapa to Tulancingo and Hausteca), is collected by Indians and marketed in Mexico City, where it is used for candle-making.

The myrica fruits are of the size of a pea, and are covered with a snow-white crust of fat, which is permeated with brown or black spots.

The method of preparing the wax is a very primitive one, and consists in boiling the berries in water, when the melted fat rises to the top. This is skimmed off, poured into shallow vessels, and crudely purified by remelting over water.   One shrub furnishes 10-15 kilos. of berries, yielding on a practical scale about 20 per cent of myrtle wax.   The

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[1] Wimmel, *Zeit. d. öst. Apothekervereins*, 1867, v. 350.
[2] *Journ. Soc. Chem. Ind.*, 1897, 247.   [3] *Ibid.*, 1898, 14.
[4] In the *Bull. Imp. Inst.*, 1906, 301, the statement was made that no proper organisation exists as yet for collecting the myrtle berries in Cape Colony.   Since then the Cape Government has leased the Crown lands on which the berries used to be collected.   The result has not, however, so far been satisfactory, and the quantities exported have decreased.

commercial myrtle wax has a green colour (due to chlorophyll ?) ; on exposure to the air the uppermost layers are bleached to a whitish mass.

Smith and Wade[1] confirmed *Chittenden and Smith's*[2] earlier statement that the myrtle wax fatty acids consist chiefly of palmitic acid. By recrystallising myrtle wax four times from petroleum ether, *Smith and Wade* obtained pure palmitin of the melting point 62·5° C., saponification value 209·4, and refractive index 1·4380 at 80° C. They further showed that by following *Hehner and Mitchell's* method no stearic acid was obtained. Judging from the low iodine value, only small proportions of olein can be present.

Smith and Wade observed notable changes in the melting point ; in the course of four months there occurred a rise of 4·45° C. in the melting point. This phenomenon may be explained by the freshly melted palmitin having been converted, on standing, into its crystalline form (cp. Chap. I.).

The acid values of two specimens of myrtle wax examined by *Deering* were 3 and 4·4. The acid value of the specimen examined in the author's laboratory was 3·6. The amount of unsaponifiable matter found by *Cocking*[3] was 2·51 per cent.

Myrtle wax worked up by itself does not yield useful candles ; it can, however, be employed in a proportion of 20-25 per cent as an addition to other candle material. In the United States " beeswax " candles are made which contain a notable amount of myrtle wax. Myrtle wax should prove useful in the manufacture of soap. In this connection it may be mentioned that *Chevreul* first prepared myrtle wax soap on a laboratory scale.

[1] *Journ. Amer. Chem. Soc*, 1903, 629.
[2] *Amer. Chem. Journ.*, 1884 (6), 217 ; *Bull. Imp. Inst.*, 1906, 365
[3] *Chemist and Druggist*, 1908, 74.

Physical and Chemical Characteristics of Myrtle Wax

Specific Gravity		Solidifying Point		Melting Point		Saponification Value		Iodine Value		Reichert Meissl Value.		Refractive Index	
At °C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms KOH.	Observer.	Per cent.	Observer.	c.c. 1/6 norm. KOH.	Observer.	At 80° C.	Observer.
15 — 0·995 22 — 0·9806	Allen Smith and Wade	39-43 45	Allen Smith and Wade	40·44 48	Allen Smith and Wade	205·7-211·7 217	Allen Smith and Wade	1·95 3·9	Lewkowitsch Smith and Wade	0·5	Smith and Wade	1·4363	Smith and Wade
98-99 — 0·875 (water at 15·5=1)	Allen					212 3	Cocking						
99 — 0 878 (water at 15·5=1)	Smith and Wade												

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Solidifying Point		Melting Point		Mean Molecular Weight	
Per cent	Observer.	°C.	Observer.	°C.	Observer.		Observer.
89·7[1]	Cocking	46	Allen	47·5 48 5	Allen Cocking	243 241·4	Allen Cocking

[1] It is doubtful whether 89·7 includes the amount of unsaponifiable.

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Dika Fat Group

(a) DIKA FAT, DIKA BUTTER, DIKA OIL, OBA OIL, WILD MANGO OIL

Freneb—*Beurre de dika* (*etc.*).   German—*Dikafett*.
Italian—*Sego di dika*.

For table of characteristics see p. 660.

Dika fat is obtained from the seed-kernels of various kinds of *Irvingia*
(*I. gabonensis*, Aubry-Lecomte ; *I. Barteri*, Hook. fil.). (Baill.)   Also
Mangifera gabonensis is recorded in the literature as a tree yielding dika
fat, but it appears that *Mangifera gabonensis* is identical with *Irvingia
gabonensis*.   These trees, belonging to the *Irvingia* family, are indigenous
to the West Coast of Africa, from Sierra Leone to Gaboon.   They are
termed by the natives " udika," " dika," " dita," and " oba."   The
fruits are known in Gaboon as " iba."

The natives remove the shell, grind the kernels in their fresh state
with a little water, pepper, and salt, and work them up into cakes.
These cakes form a staple article of food amongst the natives ; they are
known under the name " dika bread," [1] " dika chocolate," or " gaboon
chocolate."

Another way of preserving the kernels is to crack the nuts and dry
the kernels, which split readily into halves, in the sun.   These sun-dried
kernels can be kept for a long time without undergoing deterioration.

By boiling the kernels with water and skimming off the oily layer
the natives obtain their dika butter.

The author [2] examined a considerable quantity of both nuts and
sun-dried kernels.   The seeds were stated to be those of *Irvingia Barteri*,
Hooker, and were sent from South Nigeria to the Imperial Institute.
The nuts were in so advanced a state of mouldiness that it was useless
to extract the fat from them.   Sound nuts are stated to yield from 18
to 20 per cent of kernels.

The sun-dried kernels contained 54·3 per cent of fat.   This fat was
in a comparatively fresh state, as the percentage of free fatty acids
amounted to 3·35 per cent only.

The numbers found in the examination of this sample (I.) are collated
with those of two other samples (II. and III.),[3] which contained respec-
tively 6·3 and 0·9 per cent of free fatty acids.   The kernels used for the
preparation of fats II. and III. yielded respectively 60·1 and 66·3 per
cent of fat.

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[1] An examination and illustration of "dika bread" is published by Dr. E. Heckel,
2ᵉ *Mémoire des Annales du Musée et de l'Institut colonial de Marseille* ; cp. also *Bull.
Imp. Inst.*, 1904 (iv.), No. 1.   A "dika bread " is also prepared from the roasted seeds
by mixing them with those of *Fegimaura africana*, Pierre, and of *Pentaclethra macro-
phylla*, Benth. (see "Owala Oil," p. 242).   Drabble, *Quart. Journ. Inst. Comm. Research
in the Tropics*, 1908, 20.   [2] *Analyst*, 1905, 394.
[3] *Bull. Imp. Inst.*, 1909, 373.

Physical and Chemical Characteristics of Dika Fat

Specific Gravity. At °C.		Solidifying Point °C.	Melting Point °C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index. At °C.	Acid Value.	Observer.
40 (water at 40=1)	0·9140	29·4-27·2	38·9	244·5	5·2	0·42		6·7	Lewkowitsch. I.
100 (water at 15=1)	0·863			250	3·34				,, II.
		39·2		243·8	4·2				
50	0·9125	39·9	41·3	241·2	4·3		50 1·4505	3·98	Grimme III.

Physical and Chemical Characteristics of Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable. Per cent.	Unsaponifiable Matter.	Solidifying Point °C	Melting Point.	Neutralisation Value.	Iodine Value.	Mean Molecular Weight.	Refractive Index. At °C.	Observer.
	0·73	34·8				214		Lewkowitsch
94·38	1·43	38·1	40·8	254·8	14·5	218·3	50 1·4357	Grimme

No stearic acid could be detected (*Lewkowitsch*).

The iodine value is much lower than the one given by *Dieterich* —viz. 30·9-31·3. Since *Dieterich* also records a low melting point— viz. 29°—he evidently did not have genuine dika fat in his hands. The iodine number found by the author is in good agreement with *Oudemans'* [1] statement that dika fat consists of laurin and myristin only, to the exclusion of olein. It should, however, be mentioned that tho absence of olein was only inferred by him from the fact that no ether-soluble calcium salt could be obtained. *Heckel* confirmed *Oudemans* in that he could not obtain an ether soluble lead salt; but, of course, this cannot be taken as proof for the absence of oleic acid.

Tho absence of stearic acid, the low mean molecular weight of the total fatty acids, and the somewhat large quantity of insoluble volatilo acids obtained in the *Reichert-Wollny* test, confirm in the main the composition given by *Oudemans*. A small proportion of oleine must, however, be allowed. Since *Oudemans* showed by careful examination that palmitic acid is absent, the fat may be taken as consisting of myristin, laurin, and a few per cent of olein.

Dika fat has not yet been prepared on a manufacturing scale, the difficulty of importing the sun-dried kernels being still greater than that of importing palm kernels. The fat would be useful for the soap and candle industries, and might also prove suitable for edible purposes. Indeed, *Sachs* [2] states that it is used as a " chocolate fat."

(b) TANGKALLAK FAT, TANGKALLAH FAT

French—*Suif de Tangkallak*.   German—*Tangkallakfett*.
Italian—*Burro di tangkallak*.

For table of characteristics see p. 663.

This fat is obtained from the fruits of *Lepidadenia Wightiana, Nees,* Bl. (*Cylicodaphne sebifera, Cylicodaphne Litsæa*, Bl., *Tetranthera calophylla*, Miquel, *T. laurifolia*, Jacq., *Litsæa sebifera*, Pers., *Sebifera glutinosa*, Lour.), a tree indigenous to Western Java, and at present common in Indo-China. It is also found in Réunion under the name *bois d'oiseau*.

The statements occurring in the literature regarding the chemistry of tangkallak fat are conflicting, and it would therefore appear that the several observers who have published notes on this fat, examined specimens from different species of plants. *Van Gorkom* [3] stated that the fat consists of 15 per cent of olein and 85 per cent of laurin. This was confirmed by *Oudemans*.[4] Later *Greshoff* [5] found in the fleshy

[1] *Journ. f. prakt. Chem.*, 81, 356.
[2] *Chem. Revue.* 1908, 9.
[3] *Nat. Tijdschr. Ned. Ind.*, 1858 (xviii.), 410.
[4] *Zeitschr. f. Chem.*, 1867, 256.   [5] *Teysmannia*, 1890 (1), 127.

part of the fruit of a *Cylicodaphne* 36·5 per cent of a fat, melting at 37° C., and in the seeds 52 per cent of a fat of the melting point 44° C. *Sack*,[1] by extracting the seeds with ether, found 47·3 per cent of a fat which yielded by repeated crystallisation from alcohol a glyceride melting at 45° C. This was judged by *Sack* to be pure trilaurin. From the data given by him, the author calculates the iodine value of the fat to be 11·54, which agrees fairly with his statement that tangkallak fat contains 13·4 per cent of triolein. The remaining 86·6 per cent is considered by *Sack* to be trilaurin.

Recently *Schroeder*[2] examined the fat from genuine seeds of the tangkallak tree obtained from Buitenzorg (Java). The seeds yielded 51 per cent of fat on extraction with petroleum ether. The numbers obtained by *Schroeder* are collated in the table of characteristics with those of *Sack* (see p. 663). The iodine values speak against the identity of the two specimens examined by *Sack* and by *Schroeder*. The amount of insoluble fatty acids + unsaponifiable was found by *Schroeder*, as the mean of three determinations, to be 76·1 per cent, which points to the fact that large quantities of lauric acid had been washed away. The amount of unsaponifiable matter was 1·44 per cent. The *Reichert-Meissl* value of 1·47 would appear to be due to small quantities of volatile fatty acids, lower than lauric acid, inasmuch as the saponification value of the fat ascertained by *Schroeder*—268·2—is higher than the saponification value of laurin. The fat would, therefore, appear to consist of practically pure laurin. Besides lauric acid, *Schroeder* found small quantities of a liquid fatty acid which had the iodine value 68·65 ; most likely this was oleic acid, holding in solution some lauric acid. According to *Schroeder*, tangkallak fat consists of 96·4 per cent of laurin and 2·6 per cent of olein.

The specimen examined by *Schroeder* had the acid value 3·35. The fat dissolved in 15 parts of absolute alcohol at 20° C.

Tangkallak fat is used in Java for the manufacture of candles. One tree is stated to provide annually sufficient material for the production of 500 candles.

[1] *De Indische Mercuur*, 1903, 28th April ; *Pharm. Weekblad*, 1903, 4.
[2] *Arch. d. Pharm.*, 1905 (243), 631.

Physical and Chemical Characteristics of Tangkallak Fat

Specific Gravity		Solidifying Point		Melting Point		Saponification Value	
At 41° C.	Observer.	°C	Observer.	°C	Observer.	Mgrms. KOH.	Observer.
...		...		37	Sack		
0·8734	Schroeder	27	Schroeder	46·2	Schroeder	268·2	Schroeder

Physical and Chemical Characteristics of Tangkallak Fat—continued

Iodine Value		Reichert-Wollny Value	
Per cent.	Observer.	c.c ½ norm. KOH.	Observer.
11·54	Sack [1]	...	...
2·28	Schroeder [2]	1 47	Schroeder.

[1] Calculated by the author from the proportion of triolein given by Sack.   [2] By means of iodine bromide.

weighed 360 grms., and yielded 78·14 per cent of shells and 21·86 per cent of kernels. The latter were dry, had a pleasant taste, were free from rancidity and yielded, on extraction with petroleum ether, 60·45 per cent of an almost white fat of pleasant taste (after purification). The Cambodja fats, although over two years old, were only slightly rancid.

The extracted fat, as also the native fats, had the consistence of beeswax; in contradistinction to this substance they had a crystalline structure, and hence were more friable than beeswax. The following numbers were determined in these fats by *Bontoux* :—

	Fat extracted in the Laboratory.	Native Preparations	
		No. 1.	No. 2.
Fat—			
Melting point, ° C.	39·7	38·2	38·4
Solidifying point, ° C. .	31	31·2	31·8
Saponification value .	235·0–235·6	236·3	237·4
Iodine value	6·7-6·8	4·1-4·2	4·9-5·1
Acid value .	0·89	23·5	34·9
Fatty Acids—			
Fatty acids + unsaponifiable, per cent .	91·0	93·4	93·2
Solidifying point (titer test), ° C.	36·6		36·4
Neutralisation value	253·0		250·2
Mean molecular weight	222		224

By converting the glycerides into methylesters, and fractionating the latter at a pressure of 25 mm., *Bontoux* ascertained that cáy-cáy fat consists of about 5 per cent of olein, 30-35 per cent of laurin, and 65-60 per cent of myristin.[1]

The best qualities of Cáy Cáy served formerly as an edible fat in place of butter, and cakes of such butter used to be largely sold in the markets of Saïgon and Cambodja. At present hardly any edible fat is prepared, most of the product being made into candles for local use, as described above. The crude fat for this purpose is sold under the name of Cáy Cáy wax. The importation of paraffin oil into Indo-China has, however, considerably reduced the demand for candles, and the output of Cáy Cáy fat has consequently greatly decreased.

(e) KUSU OIL [2]

French—*Huile de Kusu.*   German—*Kusuol.*
Italian—*Olio di Kusu.*

Kusu oil is contained in the fruit of the camphor-yielding tree *Cinnamomum Camphora*, Nees (*Lauraceæ*). The seeds are about 0·5

[1] *Les Matières grasses*, 1908, 1277.
[2] Tsujimoto, *Journ. Coll. Eng.*, Tokyo, Imp. Univ., 1908, 86.

cm. in diameter, and weigh on an average 0·1 grm. They contain 6·78 per cent of moisture, 42·4 per cent of fat, and 2·1 per cent of ash. The fat which was prepared in the laboratory by powdering and pressing the seeds at a somewhat elevated temperature forms a white crystalline mass, having a slight aromatic odour which recalls that of cocoa nut oil. The following characteristics were ascertained :—

Specific gravity at 25° C. .	0·9267
Specific gravity at 100° C. .	0·8760
Melting point, ° C. . . .	22·8
Saponification value . . .	283·8
Iodine value . .	4·5
Reichert-Meissl value .	0·53
Refractive index at 25° C. .	1·4517

The acid value of the sample was 4·70.

The amount of insoluble acids + unsaponifiable found was 81·8 per cent ; although 2 litres of water were used for 3 to 4 grms., the wash water still contained soluble acids. The mixed acids used in the determination of the following numbers were obtained by washing with a 10 per cent solution of common salt :—

Fatty Acids

Specific gravity at 100° C.	0·8412
Melting point, ° C. .	21
Neutralisation value .	292·8
Mean molecular weight	191·6
Iodine value . . .	5·1

From the foregoing numbers it may be concluded that the chief constituent of the oil is laurin. The fat would thus resemble cocoa nut oil and its congeners, but differs notably from them by its low *Reichert* value. The fat seems to be more nearly related to dika fat, tangkallak fat, and Irvingia butter, all of which are characterised by high proportions of laurin.

Lesser Known Vegetable Fats, see table opposite.

2. ANIMAL FATS

The fats described under this head vary in their hardness, like the vegetable fats, in inverse proportion to the amount of unsaturated fatty acids they contain, or, in other words, to the amount of iodine they absorb. Butter fat, in a similar fashion as the fats of the cocoa nut oil group, occupies an exceptional position owing to its high proportion of glycerides of volatile acids. In a system based on similarity of chemical composition butter fat would be classed with the cocoa nut

oils, but it is more convenient to retain the subdivision into vegetable and animal fats, inasmuch as these two classes can be differentiated readily by the phytosteryl acetate test.

The unsaturated fatty acids of the animal fats were until recently considered to consist of oleic acid only, and this was thought to constitute an important natural difference between vegetable and animal fats. It has, however, been shown that some animal fats contain less saturated fatty acids than oleic acid. Indeed, the presence of linolic acid has been proved in the case of lard (*Fahrion*) and hare fat (*Kurbatoff*), by identifying amongst the oxidation products of the liquid fatty acids sativic acid, and, in the case of lard, by the isolation of linolic tetrabromide (*Farnsteiner*). Furthermore, *Farnsteiner* has shown that even small quantities of linolenic acid occur in lard and tallow (for a probable explanation see below). From icebear fat 9·3 per cent of fatty acids were isolated, the iodine value of which reached as high a figure as 244·4.

We are, therefore, in a position to discriminate between drying, semi-drying, and non-drying fats, similarly as in the case of vegetable oils and fats, and also to establish among the animal oils and fats all gradations from fish and liver oils down to the hardest fats, containing very small proportions of glycerides of unsaturated fatty acids. Whilst the marine animal oils simulate the drying oils, we have a certain class of animal fats, represented by icebear fat, blackcock fat, hare fat, wild duck fat, which may be likened to semi-drying oils. Reasoning by analogy, we must ascribe these drying properties to the occurrence of fatty acids, which are less saturated than oleic acid.

The presence of highly unsaturated fatty acids in icebear fat suggests the inference that the nature of the food has great influence on the chemical composition of the body-fat. On this assumption *Voit's* opinion that each animal is characterised by a specific kind of fat is no longer tenable. Although this question would appear to belong to the domain of physiology, its discussion is germane to our subject, inasmuch as this is a matter of the greatest importance to the analyst who has obtained abnormal numbers in the examination of a lard or butter fat.

It is well known that if large quantities of one particular fat are given with the food, such fat is liable to pass into the body-fat of the animal. Thus it has been shown that the fat from dogs who were given considerable quantities of linseed oil in their food had acquired the peculiar odour of linseed oil, and exhibited distinct drying properties; again, after feeding dogs with rape oil the presence of erucic acid in the fat could be proved (*Radziejewski*). *Munk* has then shown that in dogs that had been kept on starvation rations, subsequent feeding with mutton tallow produced a deposition in the body of a fat very similar to mutton tallow.[1] *Rosenfeld* states that geese fed on potatoes yield a fat with a melting point higher than the normal one, and cites this in support of his view that fat synthesised from carbohydrates is comparatively rich in the glycerides of the saturated acids. It has further

[1] Cp. Rosenfeld, *Ergebnisse d. Physiologie*, 1901 (i.), 673.

been ascertained that hogs fed on dried fish yielded lard of a disagreeable fishy taste; moreover, such lard was less hard than that from normally fed hogs. During the last decade or two the practice of feeding the hogs (in America) on maize has produced much "softer" lards than were previously obtained, a fact which must undoubtedly be ascribed to the influence of maize oil. It has also been observed that tallow from cattle fed on oil cakes is softer, *i.e.* richer in olein, than tallow from cattle fed on grass (South American tallow, New Zealand tallow), and further that lard from hogs fed on copra showed iodine values ranging from 32·5 to 42·5.

Not only does the kind of food influence the character of the *body-fat*, but, as a general rule, the fat given in the food seems also to pass into the *milk-fat*.[1] Thus *Baumert and Falke*,[2] have shown that on feeding cows with oil-cake obtained from sesamé seed, almonds, and cocoa nut kernels, there were obtained butter fats which showed so remarkable a decrease in their proportions of volatile fatty acids (*Reichert-Meissl* values) that without further investigation the butter fats would have been declared adulterated, inasmuch as the analytical characteristics were those of a mixture of genuine butter fat with very considerable amounts of foreign fats (cp. also " Human Fat," p. 686). Similarly *Gogitidse*[3] showed that the milk-fat from goats fed liberally with linseed oil had the characteristics of a butter-fat mixed with 33 per cent of linseed oil. The above-mentioned occurrence of linolenic acid in lard and tallow must therefore be ascribed to the influence of the food on the body-fat (cp. also " Lard," p. 698; "Butter Fat," p. 824). In order to further illustrate the influence of the fat given with the food, I collate some isolated observations on the fats from certain wild animals, and contrast them with the fats from the same species in a domesticated state.

Fat from					Iodine Value.
Rabbit, wild	.	.	.	.	101·1
„ tame	.	.	.	.	64·4
Goose, wild	.	.	.	.	99·6
„ wild, held in captivity 2 years			.		67·0
„ domestic	.	.	.		67·6
Duck, wild	.	.	.	.	.	84·6
„ domestic	.	.	.	.	58·5
Hog, wild	.	.	.	.	76·6
„ domestic	.	.	.	.	66
Cat, wild	.	.	.	.	57·8
„ domestic	.	.	.	.	54·5

In the case of wild goose and wild duck, the feeding on fish satisfactorily explains the high iodine values.

As a corollary to the foregoing observations, it may be added

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[1] Cp. Zuntz and Usson, *Chem. Centralbl.*, 1900, 382; Einecke, *Mitt. d. Landw. Inst.*, 1903, 559.
[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1898 (i.), 665. For similar experiments and results obtained by feeding with rice meal, see *ib.*, 1908, xv. 33.
[3] *Zeitschr. f. Biolog.*, 1904 (45), 353.

that the fat from a chicken fed on milk approximated to the composition of butter fat (high saponification value), although it did not yield a larger amount of volatile fatty acids than ordinary chicken fat (*Zaitschek*).[1] Experiments made by *Weiser and Zaitschek*[2] on geese fed with maize showed, however, that the body-fat was not altered,[3] probably because the food was poor as regards content of fat. As a further rule it may be stated that the amount of liquid (unsaturated) fatty acids decreases as the position of the fat approaches the warmest parts of the body.[4]

Bömer[5] puts forward the opinion that it is not the fats themselves (that are given with the food) which pass into the body-fat or milk-fat, but rather the fatty acids. This would, of course, mean that the fats are hydrolysed first, that the fatty acids pass through the tissues, and that the fatty acids find glycerol there (either newly formed or derived from hydrolysed fat), which has also passed through the tissues ready to perform the synthesis of fats. Some slight support for this opinion may be found in the experiments of *Pottevin*, as also of *Twitchell* (Vol. I. Chap. II.). *Bömer* thinks that a strong argument in favour of his views (that the fatty acids and not the glycerides themselves pass into the body-fat) is offered by the fact that phytosterol given with the food does not pass into the body-fat.

The view that fats are hydrolysed to glycerol and fatty acids in the first stage of the digestive process is put forward on the strength of physiological experiments by *Levites*.[6]

Noll[7] deduces from micro-chemical examinations the fact that the fat in the epithelial cells has the same composition as that of a child, and that the fat in these cells is absorbed as glycerides.[8]

In view of the change animal fats undergo in consequence of the change of food, it became of great importance to investigate whether phytosterol, if supplied together with a vegetable fat in the food, passes into the body-fat, and may therefore occur in such body-fat side by side with cholesterol. This possibility, under certain conditions, was not excluded, since the colouring matter contained in cotton seed and cotton seed oil passes into the body-fat of hogs, and into the milk-fat of cattle fed on cotton seed cake.

Since all fodders given to domestic animals contain phytosterol, and yet all animal oils and fats examined hitherto have been proved

[1] *Pflügers Arch.*, 1903 (98), 614.

[2] *Ibid.*, 1902, 128.

[3] *Ibid.*, 1902 (93), 128. Cp. also Paraschtschuk, *Chem. Centralbl.*, 1903 (i.), 731 ; Arnold, *ibid.*, 1903 (i.), 531.

[4] Henriques and Hansen, *Bioderm. Centralbl.*, 1901, 182 ; Lemmermann and Linkh, *Landw. Jahrbucher*, 1903, 635. Exceptions to this rule have been observed by Raikow (*Chem. Zeit.*, 1904, 272) in the case of bear fat ; and in the case of horse fat by Dunlop (*Analyst*, 1907, 318). The fat taken from the kidney bed, which in most animals gives the lowest iodine value, furnished the highest figure yet recorded for horse fat, viz. 110·65 (H. Dunlop).

[5] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907 (xiv.), 93.

[6] *Biochem. Zeitschr.*, 1909, 220. *Hoppe-Seyler's Zeitschr. f. phys. Chem.*, 1906 (49), 273 ; 1907 (53), 350 ; 1908 (57), 46. Cp. also Raper, *Journ. Biol. Chem.*, 1913, 117.

[7] *Pflügers Arch.*, 1910 (136), 208.

[8] Cp. also Whitehead, *Amer. Journ. Physiol.*, 1909, 294.

to be free from phytosterol, it might have been concluded, *a priori*, that phytosterol does not pass into the food. It was, however, desirable to investigate this more fully, as through feeding with cake larger doses of phytosterol are introduced into the system than with ordinary fodder. *C. Virchow*,[1] who first inquired into this matter, has shown that on feeding animals (dogs, hogs, etc.) with cotton seed oil and peas, phytosterol could not be detected in the body-fat. Nor could *Bomer*[2] detect any phytosterol in a butter from a cow fed on sesamé, cocoa nut, and almond cakes; neither could *Fulmer*[3] and *Polenske*[4] detect it in the lards of hogs fed with cotton cake and cotton seed oil respectively, although in the last case abnormally large quantities of oil were given to the pigs (*Farnsteiner*). All the foregoing researches have been confirmed by an exhaustive enquiry of *König and Schluckebier*,[5] who carefully examined the body-fat taken from five different parts of the body of young pigs (head, back, leaf, ham, intestines) as also the fat from the liver, brain, and gall. In no case was phytosterol found, cholesterol being the only alcohol contained in the unsaponifiable matter of all these fats.

It was further of great importance to investigate whether those chromogenetic substances of cotton seed oil and sesamé oil that show the characteristic colour reactions of these two oils pass into the body-fat or milk-fat if cotton seed cake or sesamé cake is given with the food. As this question will be fully discussed under the headings of " Lard " and " Butter Fat," it need only be pointed out here that exhaustive investigations have demonstrated the fact that the chromogenetic substance of cotton seed oil does migrate into lard and milk-fat, although *Thorpe*[6] noticed that individual cows vary in their ability to pass the reacting substance into the milk-fat. As regards sesamé oil, the opinions of numerous observers are conflicting, but the evidence goes to show that under certain conditions, which are not fully known yet, the chromogenetic substance of sesamé oil migrates into the milk-fat of mammals. Quite recently *König and Schluckebier* demonstrated that on feeding pigs with sesamé cake the substance which gives the *Baudouin* reaction passes into the body - fat. This was proved by examining the fat taken from five different parts of the animal (head, back, leaf, ham, intestines) which had served for the experiment.[7]

Other influences which bear on the composition of animal fat, such as the influence of seasons, climate, mode of living, age, state of health, and idiosyncrasy of the animal, will be considered under " Human Fat," " Lard," " Tallow," and " Butter Fat."

It is also noteworthy (although of minor importance for the purposes served by this work) that the iodine values of the organ fats are

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1889, 559.

[2] *Ibid.*, 1902, 1023.

[3] *Journ. Amer. Chem. Soc.*, 1904 (26), 837.

[4] *Arbeit. a. d. Kais. Gesundheitsamt*, 1905, 567 ; cp. also Farnsteiner, Lendrich, and Buttenberg, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1906 (xı.), 1.

[5] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908 (xv.), 642.

[6] *Analyst*, 1898, 257.

[7] Cp. M. Piettre, *Compte rend.*, 1911, 487 ; C. L. Hare, *Journ. Ind. Eng. Chem.*, 1910, 264 ; and E. Abderhalden and C. Brahm, *Zeitschr. f. physiol. Chem.*, 1910.

higher than those of the connective tissue fat. *Wolcke* states the following figures :—Iodine value of the fat from the liver of the normal dog 83·1, from the heart muscle 84·9, from the kidney 78·0, whereas the iodine value of the connective tissue fat was 62·8.[1] On examination the fatty acids in these organs were found to absorb from 113 to 134 per cent of iodine ; the unsaturated fatty acids appear to undergo oxidation somewhat easily on exposure to air, thereby becoming to some extent insoluble in petroleum ether. On separating the saturated fatty acids from the unsaturated fatty acids (by the lead-salt-ether method) *Hartley*[2] obtained unsaturated fatty acids (from pig and ox liver) having iodine values from 174 to 203. The bromide test led to the conclusion that the unsaturated acids contain acids belonging to the unsaturated series ($C_nH_{2n-6}O_2$) and even $C_nH_{2n-8}O_2$. (There seems to be an analogy with the acids of the fish liver oils.) *Hartley* isolated the following acids from pig liver fat :—palmitic, stearic, and an oleic acid, differing from the ordinary oleic acid, linolic acid, and an acid $C_{20}H_{32}O_2$.

Polenske[3] recently made the interesting observation that the difference between the melting and solidifying points is constant for one and the same animal fat, whereas different animal fats exhibit different (" difference ") numbers. Thus for a number of tallows the " differences " found were 12·8°-14·7° C., for goose fat 14·0°-16·2° C., and for butter fats 11·8°-14·3° C., whilst lard is characterised by higher numbers, viz. 19·2°-20·6° C. Polenske bases on this observation a method for the detection of lard, as also of tallow, in goose fat. This method is likely to prove useful for the detection of tallow and lard in butter fat.

In this work only those animal fats which have commercial importance, or may acquire such, will be treated, *i.e.* the body and the milk fats. The fats from the active organs from liver, heart, etc., are only of interest from a physiological point of view, and will only be glanced at in passing.

I subdivide the animal fats into : (1) drying, (2) semi-drying, and (3) non-drying fats. The latter are subdivided, according to their origin into (*a*) body-fats, (*b*) milk-fats.

[1] Hartley (On the nature of fat contained in the liver, kidney, and heart), *Journ. Physiol.*, 1907 (36), 18

[2] *Journ. Physiol.*, 1909 (38), 354.

[3] *Arbeit. a. d. Kais. Gesundheitsamt*, 1907, xxvi. 3

(1) DRYING ANIMAL FATS

Fats	French	German	Italian	Source	Specific Gravity. At 15° C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent	Observer
Icebear	Ours	Eisbar	Orso bianco	Ursus maritimus	0·9256	187·9	147·0	H. Bull
Rattlesnake	Crotale	Klapperschlange	Crotalo	Crotalus durissus	0·9217	210·9	105·58	Kebler and Pancoast

(2) Semi-drying Animal Fats

Kind of Fat	Source	French	German	Italian	Specific Gravity at 15° C.		Solidifying Point		Melting Point	
					Fat	Fatty Acids	Fat °C.	Fatty Acids °C.	Fat °C.	Fatty Acids °C.
Blackcock	Tetrao urogallus	Coq de bruyère	Auerhahn	Gallo di montagna	0·9296	0·9374	...	25-28	...	30-33
Lynx	Lynx europæus	Lynx	Luchs	Lince	0·9248	0·9412	...	35	...	35·3
Wild duck	Anas boschas	Canard sauvage	Wildente	Germano reale	...	...	15-20	30-31	...	36-40
Marmot	Arctomys marmota	Marmotte	Murmeltier	Marmotta	0·9183	...	...	27	...	28·5

Semi-drying Animal Fats—continued

Saponification Value.		Neutralisation Value. Mgrns. KOH.	Reichert Value. c.c. 1⁄10 normal KOH.	Iodine Value. / Per cent.		Insoluble Acids + Unsapon-ifiable. Per cent.	Refractive Index. Butyro-refractometer.				Observer.
							Fat.		Fatty Acids.		
Fat.	Fatty Acids.	Fatty Acids.		Fat.	Fatty Acids.		°C.	"Degrees."	°C.	"Degrees."	
201·6	199·3		2·10	121·1	120	...	20	70	...	...	Amthor and Zink [1]
190·2	202·7		0·4 (R.M.)	110·6	111·8	95·8	45	55·5	35	53·9	Schneider and Blumenfeld [2]
198·5	...		1·30	84·6	...	...	40	59·4	45	48·3	Amthor and Zink
197·1	209·6		0·6 (R.M.)	109·1	105·6	95·8	...	...	...	...	Gruebler [3]

1 Zeitschr. f. analyt. Chem., 1897, 1.　　2 Chem. Zeit., 1906, 54. The acetyl value of the fatty acids was 7·67.
3 Zeit. d. oster. Vereins, 1907, No. 52.

HORSE FAT

French—*Graisse de cheval.*   German—*Pferdefett.*
Italian—*Grasso di cavallo.*

For tables of characteristics see p. 677.

Fresh horse fat (from *Equus caballus*) is of yellowish colour, and
has a buttery consistence.   On standing it separates into a solid and
a liquid portion.   In its fresh state it is neutral.   As the rendering
of horse fat is not so carefully carried out as that of other animal fats,
remnants of tissue are frequently contained therein.   Hence it readily
becomes rancid.

In a sample of kidney fat stearic acid could not be detected by
the method described Vol. I. Chap. VIII.   *Farnsteiner* isolated from a
specimen of horse fat linolic tetrabromide in a quantity correspond-
ing to 9·9 per cent of linolic acid in the fat.   The fat taken from the
kidney bed, which in most animals gives the lowest iodine value,
furnished the highest figure yet recorded for horse fat, viz. 110·65
(*H. Dunlop*).[1]

The occurrence of linolic acid satisfactorily explains the weak
drying properties this fat shows on exposure to the air.

In consequence of the increasing consumption of horse meat, horse
fat has become a commercial article.   It is used by the poorer classes
on the Continent as an edible fat in place of lard, and is no doubt used
as an adulterant of more expensive fats.   Admixture of horse fat to
tallow has been practised in slaughter-houses.   Horse fat in slaughter-
house grease is stated to be detected by the biological methods[2] of
differentiating albumen from different sources.   Of course, if the
albumen has been removed in the usual manner, this method will fail.

Horse fat of low quality is used in soap-making and the manufacture
of leather greases.[3]   A technical application of horse fat for the coating
of calcium carbide in the production of acetylene has been patented
by *J. M'Rae.*[4]

The following characteristics for horse fat from various parts of the
body[5] have been published :—

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[1] *Analyst*, 1907, 318.
[2] Wittels and Welwart, *Seifenseider Zeit.*, 1910, 1014
[3] Boutoux, *Les Matières grasses*, 1910, 2026
[4] English patent 25,046, 1905.
[5] As to the foot oil, cp p. 482.

Horse Fat from	Consistence	Colour	Specific Gravity At °C	Specific Gravity	Solidifying Point °C	Melting Point °C	Solidifying Point of Fatty Acids °C	Melting Point of Fatty Acids °C	Saponification Value	Iodine Value of Fat	Iodine Value of Fatty Acids	Reichert Value	Insoluble Acids + Unsaponifiable	Acid Value	Refractive Index Butyro-refractometer at 25° C	Observer
Kidneys	Salve-like, soft	Golden-yellow	15	0·9320	22	39·1	30-30·5	36·37	198·7	81·09	83·88	0·33	95·47	1·73	"Degrees."	Amthor and Zink
,,	,,	,,	,,	,,	,,	,,	,,	,,	,,	110·7 2 / 85·4	,,	,,	,,	,,	66	Dunlop [3] / Hehner and Mitchell / Fruhling
,,	,,	,,	,,	,,	,,	,,	,,	,,	,,	82·6	84·0	,,	,,	,,	,,	,,
Neck	Like fresh hard butter	Deep orange yellow	17·5 / 50 / 15	0·9212 / ·8897 / 0·9330	48·47 / 50	53·54 / 34·45·1	32·33	41·42	187·6 / 199·5	74·84	74·41	0·22	95·42	2·44		Amthor and Zink / Dunlop
(mane)	,,	,,	,,	,,	,,	,,	,,	,,	199·1	86·7 2	,,	,,	,,	,,	,,	,,
Leaf	Butter-like	Golden-Yellow	15	0·9319	20	36·37	31-32·5	39·40·5	197·8	90·7 2 / 81·6	83·37	0·38	94·78	1·84	61·2	Amthor and Zink
Back	,,	.	17·5 / 50	0·9159 / 0·8963	45·43	52·53	,,	,,	182·8	79·9	81·4	,,	,,	,,	61 2	Fruhling
Heart	,,	.	17·5 / 50	0·9167 / 0·8948	34·32	40·41	,,	,,	184·7	77·4	78·8	,,	,,	,,		,,

1 Capillary tube method. 2 As to the horse oil obtained from these fats cp. p. 550. 3 *Analyst*, 1907, 313.

Physical and Chemical Characteristics of Horse Fat

Specific Gravity.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value		Refractive Index. Butyro-refractometer.		Maumene Test.	
At °C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c 1/10 norm. KOH.	Observer.	At 40° C.	Observer.	°C.	Observer.
15	Filsinger	20	Lenz	197·1	Filsinger	86·1	Kalmann	1·64-2·14	Kalmann	"Degrees" 53·7	Mansfeld	46·54·2	Gill and Rowe
„	Gill and Rowe	41·8·	Kalmann	195·1-196·8	Kalmann	84	Filsinger						
	Allen	43·21				71·4-72·4	Lewkowitsch					Specific Temperature Reaction.	
98-99	Gill and Rowe					75·1-	Gill and Rowe					°C.	Observer.
100						86·3						95·8·114	Gill and Rowe

0·9189, 0·916·, 0·922, 0·861, 0·798·, 0·799

¹ Capillary tube method

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value	
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
96·97·8	Kalmann	37·3-37·7	Kalmann	37·5-39·5	Kalmann	202·6-202·7	Kalmann	83·9-87·1	Kalmann
		33·6-33·7 (Titer test.)	Lewkowitsch						

Horse Oil.—The liquid portion of horse fat is frequently prepared separately by simple filtration at low temperature. It is sold in commerce as *horse oil* or " animal oil," and should not be confounded with horses' foot oil (see p. 482). The following table contains some characteristics of horse oil (*Dunlop* [1]).

Horse fat from	Colour and Consistence.	Specific Gravity at 15·5° C.	Saponification Value. Per cent.	Iodine Value (Wijs).	Reichert-Wollny Number.	Butyro-Refractometer at 25° C. " Degrees."	Unsaponifiable Matter. Per cent.	Free Fatty Acids. Per cent.
1. Kidney bed after filtration at 13·3° C.	Orange-yellow oil	0·9212	19·63	114·85	0·35	66·7	0·68	...
2. Neck ("mane") after filtration at 12·2° C.	Lemon-yellow oil	0·9182	...	90·10	0·30	61·8	0·46	...
3. Neck ("mane") after filtration at 8·9° C.	Light yellow, part liquid	0·9184	19·56	93·11	0·20	61·8	0·50	1·20
4. Neck fat	Lemon-yellow oil	0·9211	19·63	112·85	...	66·0	0·42	0·46

The drying properties of horse oil are very marked. Thus specimens of horse oil exposed for two hours in thin layers on glass gave at temperatures 95°-97° C. sticky films, which became solid after four hours (*Dunlop*).

In consequence of its pronounced drying power horse oil is unsuitable for lubricating purposes.

HARE FAT

French—*Graisse de lièvre.* German—*Hasenfett.*
Italian—*Grasso di lepre.*

For tables of characteristics see p. 679.

Hare fat (obtained from several specimens of *Lepus timidus*) is, according to *Amthor and Zink*,[2] pale yellow to orange-yellow. It is of soft consistence, and separates on standing into a thick yellow oil and a white crystalline deposit. Even in the fresh state it has a disagreeable rancid smell, which becomes more unpleasant on standing.

[1] *Analyst*, 1907, 318.   [2] *Zeitschr. f. analyt. Chem.*, 1897, 8.

Physical and Chemical Characteristics of Hare Fat

At °C.	Specific Gravity At 15° C.	Observer	Solidifying Point °C.	Observer	Melting Point °C.	Observer	Saponification Value Mgrms. KOH	Observer	Iodine Value Per cent	Observer	Reichert Value c.c. N/10 norm. KOH	Observer	Refractive Index Butyro-refracto-meter At 40° C. "Degrees"	Observer
15	0·9349	Amthor and Zink	17·23	A. and Z.	35·40	A. and Z.	200·9	A. and Z.	102·2	A. and Z.	1·59	A. and Z.		
100	0·861	Drunel	28-30	Drunel	44-46	Drunel					Reichert-Meissl Value 2·64	Drunel	49	Drunel
50	0·9134	Kllmont	29	Kllmont	35	Kllmont	204·9	Kllmont	107·0	Kllmont				

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponfiable Per cent	Observer	Specific Gravity At 15° C.	Observer	Solidifying Point °C.	Observer	Melting Point °C.	Observer	Neutralisation Value Mgrms. KOH	Observer	Iodine Value Per cent	Observer	Refractive Index Butyro-refractometer At 40° C. "Degrees"	Observer
95·2	Amthor and Zink	0·9361	A. and Z.	36-40	A. and Z.	44-47	A. and Z.	209·0	A. and Z.	93·3	A. and Z.	36	Drunel
95·5	Drunel			39-41	Drunel	48-50	Drunel						

¹ Capillary tube method

Exposed to the atmosphere in a thin layer (*e.g.* spread on a glass plate), hare fat dries in about 8 days to a tolerably viscid varnish, becoming solid after 4 more days. The iodine number after 38 days' exposure was 19·4.

Hare fat contains linolic acid. *Klimont*[1] could only detect palmitic acid in the saturated fatty acids.

The acid value of the specimen examined by *Amthor and Zink* was, in the fresh state, 2·73, and after 6 months, 8.

RABBIT FAT

French—*Graisse de lapin.* German—*Kaninchenfett.*
Italian—*Grasso di coniglio.*

For tables of characteristics see p. 681.

Rabbit fat (from *Lepus cuniculus*) is of a dirty yellow colour ; on standing it separates into a liquid and a solid portion.

The fat from the wild rabbit differs very notably from that of the tame rabbit in its iodine absorption. On exposure to the atmosphere the fat from the wild animal dries after 7 days to a nearly solid varnish, becoming completely solid after 6 more days. After 50 days' exposure the iodine number was only 26. The fat from the tame animal does not exhibit drying properties.

The acid values of the wild rabbit fat and tame rabbit fat were 7·2 and 6·2 respectively.

As a rule, the fat of domesticated animals is richer in olein than that of wild animals, but in this case, as well as in that of the wild goose, the reverse obtains.

[1] *Monatsh. f. Chem*, 1912, 441

Physical and Chemical Characteristics of Rabbit Fat

Source.	Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert Value.		Refractive Index. Butyro-refracto-meter.	
	At °C.	Observer.	°C	Observer.	°C.	Observer.	Mgms. KOH.	Observer.	Per cent	Observer	c.c. 1/10 norm KOH	Observer.	At 40° C.	Observer.
Wild Rabbit	15	0·9393	17·22[2]	A. and Z.	35·38[2]	A. and Z	199·3	A. and Z	99·8	A. and Z.	0·7	A. and Z		
Tame Rabbit	15	0·9342	Amthor and Zink[1]	22·24[2]	"	40·42[2]	"	202·6	"	67·6	"	2·8	"		
	100	0·861	Drumel[3]	26·30	Drumel	44·46	Drumel	..	..	..	..	2·64 (Reichert Meissl Value)	Drumel	49	Drumel

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Source.	Insoluble Acids + Unsaponifiable		Specific Gravity		Solidifying Point		Melting Point		Neutralisation Value.		Iodine Value.		Refractive Index. Butyro-refracto-meter	
	Per cent	Observer.	At 15° C.	Observer.	°C.	Observer	°C.	Observer	Mgrms KOH	Observer	Per cent.	Observer.	At 40° C "Degrees."	Observer.
Wild Rabbit	..	..	0·9246	Amthor and Zink	35·36[2]	A. and Z.	39·41[2]	A. and Z.	209·5	A. and Z.	101·1	A. and Z.		
Tame Rabbit	..	..	0·9264	"	37·39[2]	"	40·42[2]	"	218·1	"	64·4	"	36	Drumel
	95·5	Drumel	..	Drumel	39·41	Drumel	48·50	Drumel	..	..	..	..		

1 Zeitschr. f. analyt. Chem., 1897, 9.   2 Capillary tube method.   3 Bull. de l'Assoc. Belge, 1896 (9), 323.

(3) Non-Drying Animal Fats

HORSE MARROW FAT [1]

French—*Mölle de cheval.* German—*Pferdemarkfett.*
Italian—*Grasso di midollo di cavallo.*

Physical and Chemical Characteristics of Horse Marrow Fat

Specific Gravity.	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.	Reichert Value.
At 15° C.	°C.	°C.	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{h}$ norm. KOH.
0·9204-0·9221	24·20 [2]	35·39 [2]	199·7-200	77·6-80·6	1·0

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity	Solidifying Point.	Melting Point.	Neutralisation Value.	Iodine Value.
At 15° C.	°C.	°C.	Mgrms. KOH.	Per cent.
0·9182-0·9289	36·34 [2]	42·41 [2]	210·8-217·6	71·8-72·2

Horse marrow fat is pale yellow. A specimen of freshly rendered fat had the acid value 1·0, and a sample three months old 0·8.

GOOSE FAT

French—*Graisse d'oie.* German—*Gänsefett.* Italian—*Grasso d' oca.*

For tables of characteristics see pp. 684, 685.

Goose fat (from *Anser cinereus*) is a semi-pellucid, pale yellow fat of granular structure. It consists of olein, palmitin, stearin, and small quantities of glycerides of volatile acids.

The proportion of soluble fatty acids varies, according to *Young*, from 0·7 to 3·5 per cent, calculated as oleic acid.

There are added in the tables some characteristics of the fat from the wild goose (*Anser ferus*); the iodine value of the latter demon-

[1] Zink, *Forschungsberichte über Lebensmittel,* etc., 1896, 441.
[2] Capillary tube method.

strates that the fat of the wild goose is richer in olein than that of the domesticated goose.[1]

Lebedeff's earlier statement [2] that goose fat consists of 70 parts of triolein and 20-30 parts of tripalmitin together with some tristearin hardly merits attention. *Klimont* [3] states that he has isolated dipalmitostearin, but as the melting point 59° C. which he found is much lower than that of the same glyceride isolated by *Bömer,* by a much more careful series of recrystallisation, and, moreover, as the proof is only based on saponification values obtained with extremely small quantities of substance, little importance can be attached to *Klimont's* statements.

Adulteration of goose fat with about 20 per cent and more of lard can be ascertained by determining the melting point and solidifying point according to *Polenske's* method (Vol. I. Chap. V.). With pure goose fat differences from 14·7 to 16·7° C. are observed, whereas by the addition of 20 per cent of lard the difference rises to 17·3 and 17·5°, and in the case of an addition of 30 per cent to even 18·3° C.

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[1] Westphal, English Patent 27,138, 1911 ; French Patent 437,145.
[2] *Zeitschr. f. phys. Chem.,* 1882, 142. [3] *Monatsh. f. Chem.,* 1909, 341.

[TABLE

Physical and Chemical Characteristics of Goose Fat

	Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
	At °C.		Observer	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
Domesticated goose	37·8 (water at 37·8=1)	0·909	Young	··	··	··	··	192·6	Valenta
,,	15	0·9229-0·9300	Rozsényi	18·1-18·4	Rozsényi	33·34	Bensemann	184-198	Young
,,	15	0·9274	Amthor and Zink	18·20	Amthor and Zink	27·5-31·7	Rozsényi	191·2-193	Rozsényi
						32·34	Amthor and Zink	193·1	Amthor and Zink
Wild goose	··		··	18-20	··	··	··		
Wild goose, 2 years in captivity	15	0·9158	,,	··	··	··	··	196	,,

Physical and Chemical Characteristics of Goose Fat—continued

	Iodine Value.		Reichert-Meissl Value.		Refractive Index.		
					Butyro-refractometer.		
	Per cent.	Observer.	c.c. N/10 KOH.	Observer.	At 40° C.	"Degrees."	Observer.
Domesticated goose	71·5	Erban and Spitzer	··	··	50	50·5	Rozsényi
,,	58·7-66·4	Rozsényi	0·2-0·3	Rozsényi			
,,	67·6	Amthor and Zink					
Wild goose	99·6	,,					
Wild goose, 2 years in captivity	67·0	,,					

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point		Melting Point.	
	Per cent.	Observer.	At 15° C.	Observer.	° C.	Observer.	° C.	Observer.
Domesticated goose .	95·88	Bensemann	...	.	...	...	37-38 and 40-41	Bensemann
,, .	92·1-95·7	Young	...		...		36·6-49·2	Rozsényi
,, .	91 5-95·3	Rozsényi	0·9257	Amthor and Zink	31-32	Amthor and Zink	38-40	Amthor and Zink
Wild goose .	...	.	0·9251	,,	33-34	,,	34-40	,,
Wild goose, 2 years in captivity	...	.			32	,,	36-38	,,

Physical and Chemical Characteristics of the Insoluble Fatty Acids—continued

	Neutralisation Value.		Iodine Value	
	Mgrms. KOH.	Observer.	Per cent.	Observer
Domesticated goose .			...	
,, .	202·4	Amthor and Zink	65·3	Amthor and Zink
Wild goose .	196·4	,,	65·1	,,
Wild goose, 2 years in captivity				

HUMAN FAT

French—*Graisse d'homme.*   German—*Menschenfett.*
Italian—*Grasso d'uomo.*

For tables of characteristics see p. 688.

Human fat was first examined by *Chevreul* and afterwards by *Heintz.*

The consistence of human fat approaches that of butter. On crystallisation from ether *Mitchell*[1] obtained a slight deposit of crystals, melting at 51·5° C.; under the microscope these crystals somewhat resembled those frequently obtained from flare lards. *Parthcil* and *Ferié*[2] obtained pure tripalmitin on removing the liquid portion by expression and crystallising the solid portion from absolute alcohol. In the liquid portion dioleo-stearin was identified. Human fat may therefore be considered as consisting chiefly of tripalmitin and dioleo-stearin ; neither myristic nor lauric acids were found by the lithium salt method. In the light of these numbers the statement made by *Jaeckle*[3] that the mixed fatty acids consist of 4·9-6·3 per cent of stearic acid, 16·9-21·1 per cent of palmitic acid, and 65·6-86·4 per cent of oleic acid must be accepted with reserve. The amount of unsaponifiable matter was found by *Jaeckle* to be 0·33 per cent; the proportion of lecithin calculated from the phosphorus contents was 0·084 per cent.

The iodine value of the fat of new-born babies was found by *Knöpfelmacher* to be 43·3.[4] The proportion of liquid acids increases, however, rapidly, until at an age of one year the iodine value of 65 (67·25 *Langer*) is found, which is the iodine value of the fat from adults. (In the case of young pigs *Konig and Schluckebier*[5] ascertained that the iodine value decreases with the age, and that the melting point of the fat increases correspondingly.) The fat of well-fed children is richer in oleic acid than that of underfed ones. The influence of food on the iodine value of the fat is further clearly illustrated by the statement made by *Rosenfeld*[6] that the fat of Polynesians, living chiefly on cocoa nuts, resembled somewhat cocoa nut oil, whereas the fat obtained from an Eskimo had the iodine value 79—thus showing the influence of the blubber oil taken in the food.

The variations in the chemical characteristics of fat from the various parts of the human body do not interest us here, and the reader must be referred to the footnotes. The following statement, if read in conjunction with the remarks made on p. 669, may, however, prove interesting. The fat taken from the muscles of the heart of a person who had been suffering from fatty degeneration of the heart, gave the following numbers[7] :—

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[1] *Analyst*, 1896, 172.   [2] *Arch. d. Pharm.*, 1893, 545.
[3] *Chem. Zeit.*, 1897, 163.
[4] *Chem. Centralbl.*, 1898 (1.). 788.   Cp. also L. Wacker, *Zeitschr. f. Physiol.*, 1912, 349.   [5] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908, 641.
[6] *Chem. Zeit.*, 1902, 1110.   [7] Lindemann, *Zeitschr. f. Biol.*, 1899, 38 ; 405.

Saponification value			.	257·4
Iodine value	.	.	.	108·55
Reichert-Meissl value				23·9
Acid value	.		.	18·35

According to *P. Hartley*[1] the higher fatty acids from the *liver*, *kidney*, and *heart-muscle* include, in addition to saturated acids and acids of the oleic series, considerable amounts of acids of the series $C_nH_{2n-4}O_2$, $C_nH_{2n-6}O_2$, and possibly $C_nH_{2n-8}O_2$. These unsaturated fatty acids yield on bromination additive products insoluble in ether, carbon tetrachloride, alcohol, and acetic acid, thus resembling the bromo-acids of the series $C_nH_{2n-8}O_2$.

Fat extracted from human hair (*Meyer*[2]) had the following characteristics :—

Specific gravity at 60° C.	0·9086
Saponification value .	200
Iodine value .	67
Reichert-Meissl value . .	2 3
Insoluble fatty acids + unsaponifiable	90 per cent
Unsaponifiable matter . .	3 per cent
Refractive index at 28° C.	1·47009

The view that the fatty body secreted by the skin contains wool wax has been shown to be erroneous by *Unna and Golodetz*.[3] Notable quantities of cholesterol were found. Isocholesterol, however, could not be detected.

When decomposition of the human body sets in, the tissue disappears first, and the more resistant fat is converted into the so-called *adipocere* (French, *Adipocire*; German, *Leichenwachs*; Italian, *Cera cadaverica*), a hard wax-like mass consisting chiefly of fatty acids (cp. Vol. I. Chap. I.), and lime soaps of fatty acids.

Adipocere was first described by *Antoine François Fourcroy*, who placed it together with cholesterol (found by *Conrad* in 1775 and by *Green* in 1788 in the biliary calculi) and spermaceti in a separate class termed " adipocere." *Schmelck*[4] examined three specimens of adipocere, with the following result :—Melting point, 62·5° C.; insoluble fatty acids, 83-84 per cent; ash, 1·64-1·79 per cent (containing 83-84 per cent CaO); unsaponifiable matter, 16·7 per cent; acid value, 197 ; neutralisation value of the fatty acids, 202·8-203·4 ; iodine value, 14-14·2 ; iodine value of the fatty acids, 14·4. According to *Tarugi*,[5] adipocere consists chiefly of palmitic acid.

With regard to fat obtained from Egyptian mummies, cp. *W. A. Schmidt*.[6]

[1] *Journ. Physiol.*, 1907 (36), 17.   [2] *Chem. Zeit.*, 1905, 1028.
[3] *Biochem. Journ.*, 1909, 489.   [4] *Chem. Zeit.*, 1902, 11.
[5] *Gazz. chim. ital.*, 34, n. 469 ; *Chem. Centralbl.*, 1905 (i.), 683.   The statement that adipocere consists chiefly of palmitic acid was first made many years ago (Wetherill, *Trans. Amer. Philos. Soc.*). Cp. also E. Salkowski, *Zur Kenntniss der Fettwachs-bidlung*, p. 20 (Festschrift f. R. Virchow, 1891, Berlin, Reimer).
[6] *Chem. Zeit.*, 1908, 769.

Physical and Chemical Characteristics of Human Fat

	Specific Gravity		Solidifying Point		Melting Point		Saponification Value		Iodine Value		Reichert-Meissl Value		Thermal Test		Refractive Index. Butyro-refracto-meter.		
	At ° C.	Observer.	° C.	Observer.	° C.	Observer.	Mgrms KOH.	Observer.	Per cent.	Observer.	c.c. ·b norm. KOH.	Observer.	Heat of Bromi-nation. °C	Observer.	At 40° C. "Degrees."	Observer.	
Adult	15	0·9170	Jaeckle [1]					193.3-199	Jaeckle			0.25-0.55	Jaeckle					
	25 (water 25°=1)	0·9033	Mitchell [2]	15	Mit-chell	17.5	Mit-chell	195.-196.25-198.1	Mitchell Parthell and Ferie	61.5 57.21-66.31	Mitchell Parthell and Ferie	0.5 1.12-2.12	Mitchell Parthell and Ferie	11.3	Mit-chell	49·6-53	Mitchell
New-born babes								204.3	Jaeckle	47.3-58.1	Jaeckle	1.75-3.4	Jaeckle				

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable		Solidifying Point	Melting Point	Iodine Value		Observer.
Per cent.	Observer.	°C	°C.	Per cent.		
95.3	Krotschman	30·5	35.5	64		Mitchell
93·92·96	Parthell and Ferie			Iodine Value of the Liquid Fatty Acids. 92·1		"

1 *Chem. Zeit.*, 1897, 168.   2 *Analyst*, 1896, 172.

LARD, HOG FAT

French --*Saindoux, Graisse de porc.* German --*Schweinefett.*
Italian---*Strutto.*

For tables of characteristics see pp. 694-696.

" Lard," originally used to denote the fat rendered from the leaf of the pig, *i.e.* the fat from the kidneys and the bowels.

The increased consumption of lard during the latter half of the last century (which has seen the rise of large American packing-houses manufacturing lard on an enormous scale), has chiefly contributed to the extension of the above-given definition of lard, so that at present *lard* denotes the fat from any and every part of the hog.

What was originally termed lard is still being sold on a small scale as " butcher's lard " and " home-rendered lard." Compared with the enormous quantities which are being produced in the slaughter-houses of America, especially in those of the United States, the amount of lard which is produced locally on a small scale has become an insignificant quantity. That produced in large municipal or private slaughter-houses no longer consists entirely of leaf lard. " Bladder-lard "---so named from the package---used to be leaf lard rendered in small establishments. This term is still used to denote the best quality of home rendered, as also of American lard of quality (c) (see below). Another quality of lard sold in the retail trade as " keg lard " (so named from the package) always contains, besides leaf lard, the fat taken from other parts of the animal.

As stated already, at present " lard " denotes the fat taken from any and every part of the hog. Implicitly this has been recently acknowledged by the Adulteration Laws of the United States, according to which the term lard is defined as the " rendered fat from slaughtered, healthy [1] hogs free from rancidity and containing no more than 1 per cent of substances other than hog fat." The production of, and trade in, lard made at present may be considered as being completely dominated by the processes and trade usages in vogue in the United States, especially in the large packing-houses of Chicago.

The rules of the Chicago Board of Trade define the following brands of edible lard :---(a) *Neutral Lard No.* 1 ; (b) *Neutral Lard No.* 2 (*Imitation Neutral Lard*) ; (c) *Leaf Lard* ; (d) *Choice Lard, Choice Kettle-rendered Lard* ; (e) *Prime Steam Lard.* These brands will be described here in the order in which they are produced, so as to give, at the same time, a concise account of the manufacturing processes involved in the production of edible lard.

In the American packing-houses, in some of which up to 10,000 hogs are killed per day, the animals are driven into a shackling pen,

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[1] This is important, as in the State of Iowa a law is in force which says that lard made from hogs that have died of disease may be sold if the fact be mentioned to the purchaser at the time of sale.

where they are fastened to a " wheel hog hoist " by means of which they are hoisted up to the " sticking pen." Immediately after they have been killed they are delivered automatically by a travelling band into a " scalding tub," from which the carcasses are thrown out and carried automatically into the hog-scraping machine, where the bristles are scraped off. The carcasses are then cut up immediately, and in the first instance the leaf (French—*panne*; German—*Liesen, Flohmen*; Italian—*sugna*) is taken out, freed from the flesh and skin, and then chopped up in fat-cutting machines into small lumps and thoroughly washed with iced water. The comminuted mass is then delivered into jacketed rendering vessels, in which it is heated up to a temperature of 40°-50° C. The lard so obtained—(*a*) *Neutral Lard No.* 1—is practically neutral, and is used almost exclusively in the manufacture of " margarine " (termed in America " oleo-margarine ").

If the leaf cannot be rendered in its fresh state it is placed in refrigerating rooms until it can be worked up. The first method can, of course, only be used in small establishments, whereas the latter method, as the author has himself seen in the Chicago stockyards, is the one practised on a large scale. Moreover, it is claimed that the so-called " animal flavour " is more efficiently removed by a prolonged cooling process.

The fat from the back [1] is rendered in a similar manner. The skin is either removed by hand or by a back-fat skinning machine. This lard is sold as (*b*) *Neutral Lard No.* 2 " Imitation Neutral Lard " (quoted on the Rotterdam Exchange as " Imitation Lard "). This fat is used in America chiefly for the purposes of confectioners and biscuit bakers. On the continent of Europe this lard finds extensive use for the same purposes, further in the manufacture of margarine, and also as an adulterant of butter (see " Butter-fat ").

Neutral Lard No. 1 and Neutral Lard No. 2 (not being " cooked ") do not keep well and cannot therefore be used like " leaf lard " and " steam lard " for domestic purposes. The author would explain this fact as being due to the enzymes (which he considers as the primary cause of the incipient stages of rancidity) not having been destroyed completely at the comparatively low temperature at which these two brands of lard are rendered.

(*c*) *Leaf Lard*, Flare Lard (" flair lard ") (German—*Speckschmalz*). —On subjecting the residue from (*a*) to steam heat under pressure, the leaf lard of commerce is obtained. Formerly this was the only kind of lard recognised by the Chicago Board of Trade, and was then prepared from the whole leaf, and thus embraced the three qualities described under (*a*), (*b*), and (*c*). This lard is not exported, but is consumed at home. The Adulteration Laws of the United States now define *leaf lard* as " the lard made from the internal fat of the abdomen,

---

[1] The back-fat lard is separated by a fascia into two layers, the outer one of which melts at a lower temperature than the inner. This peculiarity extends even so far that hogs reared in colder climates have a considerably softer (that is richer in olein) outer fat layer than the hogs reared in warmer climates. Such differences are not noticeable in the fat of the inner portions of the body.

excluding that adhering to the intestines, and having the iodine number 60." The "cracklings" from best leaf-lard are mixed with bone meal and sold as chicken food under the name of " azotine."

The portions of the leaf remaining after the rendering of *Neutral Lard No.* 1 are frequently put together with the residues obtained in the preparation of *Neutral Lard No.* 2, and rendered by steam heat either in open steam-jacketed kettles or in autoclaves. The lard so obtained consists, therefore, exclusively of the residue from *Neutral Lard No.* 2, or from a mixture of residues from *Neutral Lard No.* 1 and *Neutral Lard No.* 2. This lard is known as (*d*) *Choice Lard, Choice Kettle-rendered Lard* (French—*Saindoux de choix*). The open steam-jacketed kettles are a survival of the old-fashioned open kettle in which butchers used to render the lard over free fire. Such lard had the peculiar, pleasant flavour of fried fat and therefore the name " kettle-rendered lard " has been retained even after the rendering over free fire had given way to heating by means of steam. In large establishments the rendering is carried out under pressure (in digesters). In some establishments, however, the jacketed vessels are still in vogue ; they are usually square tanks, provided with one or more circular flue-pipes passing through the centre of the tank, so as to distribute the steam over as large a surface as possible. According to the regulations of the Chicago Board of Trade " choice lard " is defined as lard made from leaf and trimmings only, either steam or kettle-rendered ; the manner of rendering must be branded on each tierce. Its flavour is much superior to that of " prime steam lard."

After this lard has been drawn off from the autoclave, the residue, termed " tankage," is withdrawn and worked up in the fertiliser department (see Chap. XVI.).

The lowest quality of edible lard is (*e*) *Prime Steam Lard* (French—*Saindoux à la vapeur* ; German –*Dampfschmalz*), also termed " standard prime steam lard," and obtained from any trimmings not used up in the production of lard (*d*), and all other parts of the hog that will yield lard, with the exception of the liver, lungs, the intestines proper, and of that part of the heart which is free from fat, etc. This quality is rendered in digesters in a similar manner to (*d*). This lard is passed solely on inspection, and as the inspector has no authority enabling him to supervise rendering establishments in order to secure a proper control, we may take it that prime steam lard consists of the fat from any part of the hog, either from the whole animal or from portions of it (head, foot).

As stated already, these qualities are used for edible purposes only.

Lard is also used for the extraction of perfume from flowers by the " maceration process," in which the flowers are dipped in the fat previously heated to about 80° C. and expressed, the operation being repeated up to 25 times.

All those parts of the hog which have not been used for the production of edible lard—such as " guts," etc.—are worked up in autoclaves, in order to obtain the last portions of fat they contain. Such fat is known as " yellow grease " (see Chap. XVI.). With it is mixed

all the refuse fat resulting in the course of rendering the edible qualities. The " yellow grease " is generally worked up together with any hogs that have died in the " Stockyards." This quality is, of course, only used for manufacturing purposes, such as for the production of soap, low quality lard oil, or " grease stearine."

The hogs which have died in transit are rendered for fat in their entirety, after the intestines have been removed, as the fat from the latter would discolour the resulting grease. The grease so obtained is sold as " white grease " for manufacturing purposes.

The intestines which have been removed from the dead animals are worked up separately, and yield a grease sold as " brown grease." This is used for the manufacture of soaps and the lowest class of commercial lard oil.

A further kind of grease—" pig's foot grease "—is a by-product obtained in the glue department of the packing-houses. It also finds an outlet in the manufacture of low-class lard oil as a substitute for Neat's foot oil,[1] and of soap.

In this section only lard proper will be dealt with, i.e. all the edible qualities enumerated above from (a) to (e) (cp. Vol. III. Chap. XVI. " Greases ").

The two qualities of " neutral lard " hardly require any refining. After the clear melted lard has settled in the jacketed vessel, it is run off into a receiving tank, in which the last traces of water and any fibres are precipitated by sprinkling salt over the fat (cp. manufacture of " Premier Jus," Chap. XV.). The settled lard is then ready for use in the margarine department of the works, or is run into tierces for shipment.

The next qualities of edible lard usually undergo a more compli-cated process of refining. This consists in treating the melted fat in a refining vessel with fuller's earth, blowing it at the same time with air. This is done not only to mix the lard but also to deodorise those qualities which require such treatment. The treated mass is then pumped through a filter-press, from which the clear bleached lard is run over horizontal cylinders cooled by brine. In small establishments a single cooler is used ; in the large packing-houses two cooling cylinders, arranged side by side in one open tank, are usually employed. These cylinders revolve slowly in the warm lard, being immersed in it to about half their diameter. Whilst rotating they carry up a layer of lard, which is quickly chilled on the cooled surface and forms a continuous sheet of solidified fat. On the opposite side, before the cylinder dips again into the warm lard, the solidified mass is removed by a scraper and falls into a trough. In this trough a rotating screw conveyer breaks up the sheet of fat and carries it forward into a mixer, in which the lard is agitated by a mechanical arrangement. Here lard stearine is added, if need be, to " stiffen " soft lard.

At this stage of the process such ingredients as are incorporated with lard in the manufacture of " Lard Substitutes " (see Chap. XV.) are also added.

[1] Fabrion, *Zeitschr. f. angew. Chem.*, 1911, 1318.

The finished product is taken off by a pump, which delivers the semi-solid mass through a range of strainers into the vessels (" tierces ") in which the lard is shipped.

The object of the agitation of the lard is to produce rapid solidification of the mass, whereby a whiter product is obtained than if the lard were allowed to solidify slowly. Frequently the lard is blown at the same time with air, which, becoming entangled during the agitation, assists in giving a whiter colour to the lard. This final treatment in the agitator imparts the smooth, salve-like consistence, and also prevents the formation of crevices in the finished product which not only render the lard unsightly, but also increase the liability to rancidity by the more ready access of air. The mixing in the agitator and the blowing with air require careful observation. If not carried to a certain point, liquid portions would separate out in the tierces. The author has not infrequently noticed pools of fluid fat in tierces containing lard of a low melting point.

The machinery used in the large American packing-houses has served as a type to those European establishments where considerable quantities of lard are produced (*e.g.* in Vienna). Slight alterations are introduced into the system of cooling, as the quantities produced are not always large enough to permit the installation of brine-cooled cylinders. In such cases the hot lard is worked off in mixing machines between rollers where lard in solid form is introduced in order to induce more rapid solidification, or even lard stearine to " stiffen " the lard. Just as in the manufacture of lubricating greases and vegetable butters, the object of passing the lard between rollers is to give it a smooth appearance. With regard to the manufacture of " Lard Stearine " and " Lard Oil " see p. 741.

Reliable figures representing the extension of the lard trade in the United Sates of America, Canada, etc., are not available, but some information may be gathered from the following data :—In the year 1899 the quantity of neutral lard consumed in the production of margarine (oleomargarine) amounted to 31,297,251 lbs. In addition to this there is the consumption of lard in the United States and the amount used in the production of lard compounds (see Chap. XV., " Lard Substitutes "). The bulk of the lard is, however, exported to Europe.

Physical and Chemical Characteristics of Lard

°C.	Specific Gravity	Observer	°C. (Solidifying Point)	Observer (Solidifying Point)	°C. (Melting Point)	Observer (Melting Point)	Mgrms. KOH (Saponification Value)	Observer (Saponification Value)
15	0·934-0·938	Dieterich	27·1-29·9	Goske	42·48	Koenigs	195·3-196·6	Valenta
40	0·8985	Allen			45·46	Bensemann	195·2-196·2	Lewko-witsch
(water at 15·5=1)					36-45·5	Dieterich		
50	0·89159-0·90088	Fairley and Cooke			(Cp. p. 708)	Lewko-witsch		
(water at 50=1)								
90	0·894-0·897	Dieterich			,,	,,		
98-99	0·8608	Allen				Dunlop		
(water at 15·5=1)								
100	0·861	Koenigs						
(water at 15=1)								
100	0·8610-0·8614	Gladding						
100	0·8589-0·8641[1] (American)	Dennstedt and Vogtlander						
(water at 15=1)								

Fat from Wild Boar

°C.	Specific Gravity	Observer	°C. (Solidifying Point)	Observer (Solidifying Point)	°C. (Melting Point)	Observer (Melting Point)	Mgrms. KOH (Saponification Value)	Observer (Saponification Value)
15	0·9124	Amthor and Zink	22-23	Amthor and Zink	40·44	Amthor and Zink	195·1	Amthor and Zink
			27·9-30·8[3]	Richardson[2]	32-37·5[3]	Richardson		
			24·7-27·3[4]	,,	32[4]	,,		

1 In one case 0·8700 was found.   2 *Journ. Amer. Chem. Soc.,* 1904, 872.   3 From leaf.   4 From back.

Physical and Chemical Characteristics of Lard—continued

Iodine Value		Reichert-Meissl Value.		Maumené Test.	Refractive Index.	
Per cent.	Observer.	c.c. 1/10 norm. KOH.	Observer		At 60° C	Observer.
49·9-63·8	Dieterich	0·49-0·77	Fendler	(See Table, p. 715.)	1·4539	Thorner
62·4 (American)	Schweitzer and Lungwitz					
60·4-70·4 (American)	Raumer					Oleo-refractometer.
59-68·4 (American)	Dennstedt and Voigtlander				"Degrees."	Observer.
55 (European)	,,				-12·5	Jean
53-76·9	Lewkowitsch					
58·1-85 (Chinese)	Farnsteiner					Butyro-refractometer.
(Cp. also pp. 711-713)						

Fat from Wild Boar

Iodine Value Per cent.	Observer.	c.c. 1/10 norm. KOH.	Observer
76·6	Amthor and Zink	6·68 (R.)	Amthor and Zink
78·8-82¹	Richardson		
81·5-84·7²	,,		

Butyro-refractometer.

At °C.	"Degrees."	Observer.
25	56·8-58·5	Spaeth
40	50-51·2	Benedikt and Wolfbauer
,,	48·6-51·2	Mansfeld
,,	44·8-53	Dennstedt and Voigtlander
,,	48·1-50·7	Dunlop³
,,	53·3-54·2	Farnsteiner⁴
,,	53·8-57·3	,,⁵

¹ From leaf. ² From back. ³ Fats from different parts of the body: cp. *Journ. Soc. Chem. Ind.*, 1906, 458.
⁴ Chinese lards. ⁵ Japanese lards.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

	Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.		Mean Molecular Weight.		Iodine Value.		Thermal Test. Heat of Bromination.		Refractive Index.	
	Per cent.	Observer.	°C.	Observer.	°C.	Observer.	°C.	Observer.		Observer.	Per cent.	Observer.	°C.	Observer.	At 60° C.	Observer.
	95·8	Bensemann	99° (water 15·5=1)	Allen	34	Mayer	35	Mayer	278	Allen	64·2	Williams	10·4-11	Hehner and Mitchell	1·4895	Thörner
			0·837-0·840		39	Allen	44	Allen			Iodine Value of the Liquid Fatty Acids.				Oleo-refractometer.	
					39	Terrell	43	Terrell							"Degrees."	Observer.
					41·45-42 (Thiertest)	Lewkowitsch	43·44 and 46·47	Bensemann			89·4-90·7 (European)	Dieterich			−30	Jean
					36·02	„					93·96 (European)	Wallenstein and Finck			Butyro-refractometer. (See p. 716.)	
											108-105 (American)	v. Raumer			Refractive Index of the Liquid Fatty Acids.	
											96·9-108·2 (American)	Bömer				
											93·5-103·7 (European)	„				
											95·2-104·9 (American)	Lewkowitsch			Butyro-refractometer.	
											92-115·2 (European)	Tortelli and Ruggeri				
											97·63	Farnsteiner			At 40° C.	Observer.
											99·84 (American)	„			43·1-44·7	Bömer
											113-121·7 (Chinese)				44·45	Mansfeld
											124·2-133·7 (Japanese)					*
Wild boar			15	Amthor and Zink	32·5-33·5	Amthor and Zink	39·40	Amthor and Zink	275·5·1	Amthor and Zink	Fatty Acids. 81·2	Amthor and Zink				
			0·9333													

1 Calculated from saponific. value 203·6.　2 Iodine value of lard 76·9.　3 Genovese lard of iodine value 57·8.　4 Iodine value of lard 63·2.

The exports of lard from the United States in lbs. and their value in dollars is given in the following table :—

Year.	Lbs.	Dollars.
1896	509,534,256	33,589,851
1897	568,315,610	29,126,485
1898	709,344,045	39,710,672
1899	711,259,851	42,208,465
1900	661,813,663	41,939,164
1901	611,357,514	46,560,148
1902	556,840,222	52,375,864
1903	490,755,821	50,854,501
1904	561,302,643	46,347,520
1905	610,238,899	47,243,181
1906	741,516,886	60,132,091
1907	..	57,497,980
1908	603,413,770	54,789,748
1909	528,722,933	52,712,569
1910	362,927,671	43,301,156
1911	476,107,857	52,509,217
1912	532,255,865	52,090,441

The quantity of " lard compounds " and " lard substitutes " exported from the United States will be given in Chapter XV. under the heading " Lard Substitutes."

The following figures state the value in pounds sterling of the imports into, and the re-exports from, the United Kingdom of lard and imitation lard (see above), and also of " lard substitutes " :—

Year.	Imports of		Re-Exports of	
	Lard.	"Imitation Lard."[1]	Lard.	"Imitation Lard"[1]
	£	£	£	£
1898	2,887,801	89,025	674,828	11,875
1899	3,068,975	90,010	810,903	4,332
1900	3,266,582	98,629	480,797	2,276
1901	4,037,689	154,239	551,512	1,453
1902	4,118,992	284,830	155,457	6,548
1903	3,870,774	306,633	189,982	1,202
1904	3,342,389	238,668	194,159	1,652
1905	3,692,573	269,098	419,257	4,005
1906	4,361,399	358,492	401,743	8,500
1907	4,491,539	408,192	379,481	5,805
1908	4,407,410	306,700	256,272	2,145
1909	4,858,026	438,909	632,782	1,986
1910	4,520,074	603,444	383,907	4,652
1911	4,251,758	360,878	504,984	5,790
1912	4,573,136	434,623	580,021	3,384

Very large quantities are shipped to the French ports ; and to

[1] This term including besides "neutral imitation lard" (see above) also lard substitutes.

Rotterdam, which is the chief port for the importation of lard into Germany.

A reliable estimate as to the European production is at present impossible. The author, from information placed at his disposal, estimated that the value of lard produced in the United Kingdom was about £1,100,000 in 1902. Large quantities of lard are produced on the Continent in Roumania, Servia, Hungary, and Austria. Hardly any lard can be imported into Hungary and Austria in consequence of the enormous import duty on this article.

Leaf lard has a granular texture and a salve-like consistence and should be of pure white colour. The lards which represent mixtures from all parts of the body, especially those manufactured in large slaughter-houses, have no longer a crystalline texture, as the object of the last operation in the manufacture is to destroy such texture and give to the produce a smooth appearance.

The lard rendered from the leaf and also that from the back have an agreeable taste. The lower qualities have an insipid taste; this disappears, however, on standing. Some of the steam lards have an "animal flavour," which may be judged by an inexperienced person as indicating admixture with tallow or beef "stearine." This flavour also disappears on standing or on warming.

Leaf lard is the hardest; the lards from the back, etc., are softer (see below under "Melting point," p. 708). The consistence of a lard is not only conditioned by the part of the animal from which it has been taken, but depends also on the food which has been given to the animal. Hogs fed exclusively on acorns yield a harder lard than hogs fed on maize.

Lard consists of the glycerides of lauric, myristic, palmitic, stearic, and oleic acids, and small quantities of linolic acid (and perhaps also of linolenic acid). Volatile acids are absent, as may be seen from the low *Reichert-Meissl* value. The proportion of stearic acid in a number of commercial lards (determined by the method described, Vol. I. Chap. VIII.) varied from 6 to 24·91 per cent. The statement made first by *Fahrion*, viz. that lard contains linolic acid, is confirmed by the fact that the liquid fatty acids of lard, especially of American lards, have iodine values varying from 93 to 106, and reach even 115·5, as the author has ascertained. "Daturic" acid, stated by *Kreis and Hafner* to occur in lard as a mixed glyceride "daturodistearin," has been shown to consist of a mixture of solid acids (see below).

Bomer [1] solated by fractional crystallisation about 3 per cent of palmito-distearin and 2 per cent of stearo-dipalmitin. No evidence could be obtained for the presence of a heptadecylic acid.

By reducing lard in the presence of colloidal palladium (Vol. I. p. 59) *Paal and Roth* obtained a white mass of tallow-like consistence which melted at 56-60° C.

Farnsteiner found in a specimen of European lard (of the iodine value 51·4) the following percentages of solid and liquid acids :—

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1913, 321.

	Solid Fatty Acids.	Liquid Fatty Acids.
	Per cent.	Per cent.
Lard I. (iod. val. 51·4) .	41·3	53·7 (iod. val. 93)
,, II. . .	42·2	53·1

The 53·1 parts of liquid fatty acids of specimen II. were resolved by the barium-salt-benzene method into 39·2 parts of oleic acid and 13·9 parts of less saturated acids. The presence of linolic acid was proved by the isolation of linolic tetrabromide. Since a brominated acid of the melting point 165° C. was isolated, the inference is justified that this product represents a mixture of linolic tetrabromide and linolenic hexabromide.

Twitchell [1] calculated the composition of a lard (iodine value of the mixed fatty acids = 62·57) as follows :—

	Per cent.
Linolic acid . . .	10·06
Oleic acid . . .	49·39
Solid acids (difference) .	40·55

The iodine values of the two fractions of liquid acids he prepared were 109·35 and 118·20.

The composition of an American lard, absorbing 65·78 per cent of iodine, was examined by *Partheil and Ferié*,[2] by their lithium salt method. The analysis detailed in the third edition of this work (p. 780) is not reproduced here, as the correctness of the method is open to doubt.

On treating lard with 95 per cent alcohol some glycerides richer in olein than the bulk pass into the alcohol. As this behaviour is of importance for the detection of more readily alcohol-soluble oils and fats (such as cocoa nut oil) in lard (cp. p. 724), the results of several experiments made by *Arnold* [3] are appended. 150 grms. of lard were heated with 110 c.c. of 95 per cent alcohol for an hour on the water bath under a reflux condenser, and the mass then allowed to stand for 4-5 hours at 12-14° C. In the following table some characteristics of (I.) the original lard, (II.) the alcohol-soluble portion, and (III.) the alcohol-insoluble portion are collated :—

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[1] *Journ. Soc. Chem. Ind* , 1895, 515 ; cp. 2nd edition of this work, p. 567.
[2] *Arch. d. Pharm* , 1903, 566.
[3] *Zeits f. Unters. d Nahrgs. u Genussm.*, 1907 (XIV), 179.

	Butyro-refractometer at 40°C. "Degrees."	Saponification Value.	Reichert-Meissl Value.	c.c. N/10 KOH required for Insoluble Volatile Acids Polenske's method.	Iodine Value.	Insoluble Fatty Acids.			Yielded Alcohol-soluble portion.
						Butyro-refractometer at 40°C. "Degrees."	Neutralisation Value.	Iodine Value.	
American Lard									
I. Original Lard . .	50·1	194·9	0·33	0·55	62·5	36·7	204·4	64·2	...
II. Alcohol-soluble Fat .	52·7	190·5	0·66	0·55	68·0	40·6	200·1	73·4	9·1 g.
III. Alcohol-insoluble Fat	50·9	196·0	0·44	0·50	60·4	37·0	205·0	62·0	...
German Lard									
I. Original Lard . .	47·7	193·8	0·55	0·50	49·0	34·5	202·3	50·9	...
II. Alcohol-soluble Fat .	49·2	189·9	0·88	0·70	63·9	38·0	200·4	66·1	6·9 g.
III Alcohol-insoluble Fat	47·8	196·0	0·65	0·55	47·8	34·0	203·8	49·4	...
German Lard									
I. Original Lard . .	48·4	195·7	0·44	0·60	53·2	34·1	204·3	53·9	...
II Alcohol-soluble Fat .	51·4	191·5	0·88	0·75	66·1	38·9	200·6	67·2	6·4 g.
III. Alcohol-insoluble Fat	48·3	196·1	0·55	0·55	51·7	33·7	203·9	52·2	...

The analytical differences between lards from different parts of the hog are summarised in the following tables. Since important differences exist between North American and European lards, owing to the modes of fattening the hogs, I consider it useful to differentiate as far as possible between European and American lards.

European Lards

| Fat from | Spec. Grav at 100° C. (Water 15=1.) | Melting Point of Fat. | Melting Point of Fatty Acids. | Iodine Value of | | Free Fatty Acids. | | Observer. | Remarks. |
				Fat	Fatty Acids	c.c. norm. KOH per 100 grms.	Calculated to Oleic Acid.		
		°C.	°C.				Per cent		Mean results from examination of fats from 8 animals.
Back	0·8607	33·8	40	60·58	61·90	0·54	0·152	Spaeth	
Kidney	0·8590	43·2	43·2	52·60	54·20	0·58	0·163	,,	
Leaf	0·8588	44·5	42·9	53·10	54·40	1·28	0·360	,,	

North American Lards

| Fat from | Specific Gravity at 100° C (Water at 15° C.=1.) | Iodine Value | Maumené Test from 40° C. | Melting Point (Bensemann's Method). | | Refractive Index | Observer. |
				Drop formed at °C.	Melted to a clear drop ° C.	Butyro-refractometer at 40° C.	
			°C.			"Degrees."	
Head	0·8637	66·2	33	24	44·8	52·6	Dennstedt and Voigtlander
	0·8629	66·6	32	24	44·8	52·5	
	0·8631	65·0	34	24	45·0	52·0	
Back	0·8611	61·5	37	28·5	48·5	52·4	
	0·8621	65·0	35	28·5	48·5	51·8	
	0·8616	65·1	38	31·5	46·0	51·9	
Leaf	0·8637	62·2		26	45	51·4	
	0·8615	59·0		29	44	50·2	
	0·8700	63·0	30	28·5	44·5	52·0	
Foot (hoof)	0·8589	68·8	.	24	40	44·8	
Ham	0·8641	68·4	38	26	45	51·9	
	0·8615	66·6		26	44	51·9	
	0·8628	68·3		26	44·5	53·0	
Ham (German)	0·8597	55·0	30	32	46	49·2	Dennstedt and Voigtlander

The following table due to *Durier* [1] may be given here. No. 1 represents the lard from hogs fed on milk, chestnuts, and acorns, while No. II. is derived from hogs fed on milk, potatoes, and barley.

Fat from	Oleo-refracto-meter. At 45° C.		Butyro-refractometer. At 45° C.		Refractive Index. At 45° C.		Iodine Value.		Free Fatty Acids. Per cent.	
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
Mesentery	- 13·5	- 15·5	45·2	44·4	1·4560	1·4555	49·65	46·19	0 541	0·462
Caul .	- 13	- 15	45·4	44·6	1·4561	1·4556	49 65	46·67	0·313	0·307
Flair .	- 13	- 14	45·4	45	1·4561	1·4559	50 54	47 60	0·217	0·257
Ham .	- 12	- 12	45·7	45·0	1·4564	1·4563	53·59	52·53	0 352	0·397
Heart	- 11	..	46·1	..	1·4566	..	55·37	..	0·271	..
Breast	- 9	- 8·5	46·2	47	1·4571	1·4573	58·67	58·64	0 217	0·282
Back ⎰ outer	- 10	- 7	46 4	47·5	1·4560	1 4576	57·91	59 65	0·149	0 205
⎱ inner	- 13	- 10 5	45·4	46·2	1·4561	1·4567	54 61	55·08	0 149	0·231
mixture	- 11	- 9·5	46·1	46·6	1·4566	1·4570	56 64	57·37	0·149	0 231
Head	- 8	- 5	47·2	48·2	1·4574	1·4581	61·46	67·53	0 217	0·257

As a corollary I add the following table, setting out the percentages of stearic acid in lards taken from different parts of a hog :—

Fat from	Melting Point °C.	Iodine Absorption.	Stearic Acid		Observer
			Per cent	Melting Point °C	
Head	34·8	67·7	8·67-9·47	67·8-66·2	Hehner and Mitchell
Ham	34 6	61·6	8·74-9·02	67 5-67·3	,, ,,
Breast	36·8	64·2	11·84-10·9	67·2-66·8	, ,,
Flare	40·0	52·8	15·7-14·4	66·5-67·2	,, ,,
Back	35·6	67·9	8·59-9·2	67-66·5	,, ,,
Kidney bed	50	53·4	19·2	.	Dunlop
?	37-40	58·6	22·3	.	Kreis and Hafner
?	...	45·6	24·9	...	Hehner

Lard derived from " oily hogs " differs from ordinary lard, as is shown by the following table, due to *Richardson and Farey*.[2]

[1] *Ann. des falsific.*, 1909, 491
[2] *Journ. Amer. Chem. Soc*, 1908, 1191

Kind of Fat.	FAT							INSOLUBLE FATTY ACIDS.					
	Melting Point.		Saponi-fication Value	Iodine Value.[1]	Refractive Index.		Free Acid (as Oleic). Per cent.	Melting Point (Titer Test). °C.	Liquid Fatty Acids. Per cent.		Iodine Value.[1]	Refractive Index. At 60° C.	Bromides Insoluble in Petroleum Ether at 8° C. Per cent.
	Open Capillary Tube, lower limit. °C.	Closed Capillary Tube, upper limit, completely clear °C.			At 40° C	At 60° C.			Calcu-lated to Fat.	Calcu-lated to Fatty Acids.			
Back fat	−1·5	12·0	189·0	93·9	1·4620	1·4541	0·16	21·2	84·4	89·4	104·5	1·4452	..
Leaf lard	−1·6	17·0	191·0	95·2	1·4620	1·4540	0·16	21·6	84·2	89·2	106·8	1·4452	..
Leaf lard	−0·8	22·0	192·5	92·6	1·4621	1·4542	0·26	23·8	81·5	86·3	110·0	1·4453	..
Leaf lard	+0·9	21·0	190·5	93·8	1·4621	1·4542	0·14	23·4	82·9	87·8	106·9	1·4448	..
Ham fat	0·0	18·0	189·0	92·8	1·4620	1·4540	0·20	21·8	82·2	87·1	108·3	1·4450	1·51[2]
Ham fat	−2·4	13·0 ●	190·5	95·1	1·4640	1·4560	0·16	19·3	81·1	85·9	109·7	1·4455	..

[1] Determined with iodine bromide.   [2] Not obtained in a crystalline condition.

Pure lard contains small quantities of unsaponifiable matter. *Allen and Thomson* found 0·23 per cent, *Lewkowitsch* 0·35 per cent. The bulk of the unsaponifiable matter consists of cholesterol. It should be noted that the cholesterol can be readily obtained in well-formed crystals. As to the importance of the amount of unsaponifiable matter in the examination of lard for adulterants, see below, p. 719.

Freshly rendered lard is practically neutral ; determinations made by several chemists of the free fatty acids gave the following numbers :—

Free Fatty Acids as Oleic Acid.	No. of Samples.	Observer.
Per cent.		
0·280-0·420	?	Dieterich
0·350-1·000	12	Wiley
0·098-0·564	21	Spaeth

Lard used in pharmacy and perfumery is usually preserved by " benzoating," *i.e.* by adding a small proportion of gum benzoin which apparently arrests the progress of hydrolysis.

The increase of acidity on exposure to air in loosely-corked flasks is numerically shown in the following table, together with the fluctuations in the iodine number (*Spaeth*) :—

No.	Free Fatty Acids; c.c norm. KOH per 100 grms			Iodine Value.			
	Freshly rendered.	After one year.	After three years	Freshly rendered.	After one year.	After three years.	
						Fat	Liquid Fatty Acids.
1	0·6	6·4	32·0	63·25	53·80	39 26	74·51
2	0·45	2·75	23·0	61·15	55·45	39·37	71 60
3	0·75	7·80	31·6	62·90	51·85	39 56	72·48
4	0·80	11·60	50·0 [1]	62 95	48 80	29 41	
5	1·25	6·70	36 0	57·25	49·40	26 51	64·30
6	0·35	6·00	30·0	55·88	47·80	31·19	
7	0·45	8·40	23·0	60·10	51·04	41·08	69·20
8	0·55	21·20	41·3	55·80	37·50	22 97	
9	1·45	1·80	10·0	52·30	52·20	40·91	
10	0 55	9·60	30 0	57·08	46·70	33·69	
11	1·60	15·40	46·0	51·75	36·71	21·56	
12	0·65	9·60	33·0	63·61	49·00	38·04	
13	0·60	4·20	18·0	52 35	46·85	36·48	
14	0·50	7·60	32·0	60·95	52·72	36·03	

The free fatty acids were separated into soluble and insoluble acids by washing the lards with hot water. Their relative proportions were measured by the amounts of normal alkali required to saturate the free acids. The following table gives the details :—

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[1] Corresponding to 14 per cent of oleic acid.

No.	Free Fatty Acids after three years' exposure c.c. normal Alkali per 100 grms.	Soluble Fatty Acids c.c. normal Alkali per 100 grms.	Insoluble Fatty Acids.[1] c.c. normal Alkali per 100 grms.
1	32·0	4·5	27·5
2	23·0	4·7	18·3
3	31 6	4·2	27·4
4	50 0	8·1	41 9
5	36 0	6 6	29 6
6	30 0	1 0	26 0
7	23 0	3·1	29·6
8	11 3	7·4	33 9
9	10·0	1·9	8·1
10	30·0	3·9	26 1
11	46·0	7·1	38·9
12	33·0	4·1	28·9
13	18·0	2·1	15·9
14	32 0	4·4	27·6

Lard (like butter and olive oil) used to be adulterated on the largest scale. Beef fat, beef stearine, cotton seed oil, cotton seed stearine, and other vegetable oils were the adulterants most frequently employed. In the United States of America admixture with foreign fats and oils had become an open acknowledged practice, nay, it had even been claimed that the addition of cotton seed oil constituted an improvement in the manufacture. Thus the American brand " refined lard " was found to be a mixture of lard with cotton seed oil, and a sufficient quantity of beef stearine to obtain the consistence possessed by pure lard. Owing to the interference of the law in this and in other countries, the name " refined lard " has been abandoned, and has been replaced by such terms as " compound lard " or " lard compound." Some of these artificial preparations did not even contain any lard at all, being judiciously prepared mixtures of beef stearine and cotton seed oil or cotton seed stearine. These are now sold as " lardless beef " and under a variety of other fancy names (see Vol. III. Chap. XV. " Lard Substitutes ").

Water, which was often used as an acknowledged admixture, is not common at any rate in American lards imported into Europe. Adulteration of this kind may be practised on a small scale, but is of little importance commercially. It may, however, be stated that in some countries lard containing water is demanded by the buyer. Thus for export to Cuba, lard is prepared which contains 25 per cent of water. In this case water cannot be looked upon as an adulterant as the admixture is openly acknowledged. Lard so prepared was sold a few years ago in Europe as a butter adulterant under the name of " lardine."

In Austria refined cocoa nut oil is largely used as an adulterant, sometimes in conjunction with tallow.

[1] Evidently found by difference.

Polenske [1] ascertained that lard dissolves about 0·45 per cent of water at 96° C., and 0·15 per cent at 42° C. (which may be looked upon as the average melting point of lards) ; in both cases transparent liquids were obtained. If a larger quantity of water be present, the lard is no longer able to hold it in solution, and forms then, according to the proportion of water present, either a turbid liquid or two layers, water separating out as a lower layer. Larger amounts of water than those stated above must be considered as not permissible. (*Polenske* determines, with the aid of an empirical table, small quantities of water in lard by observing the temperatures at which a melted lard remains clear.)

I shall consider here chiefly the sophistication of lard with vegetable oils (notably cotton seed oil and cotton seed stearine) and beef stearine. With regard to the latter it should be mentioned that the admixture of 5 per cent of beef stearine, as a " stiffener," was openly advocated by the trade as a necessary operation. Such admixture is now considered under the regulations of the " *Foods and Drugs Acts* " of the different countries as an adulteration. In order to " stiffen " soft lard, lard stearine (see p. 741) is now used. The employment of the latter did not come into vogue previously, as it requires four to five times as much lard stearine as it formerly took of beef stearine to obtain the desired consistence.

In the chemical examination of a sample of lard very little importance should be attributed to the outward appearance, which was stated some years ago to offer a ready means of differentiating adulterated from genuine lard, the adulterated lard being supposed to exhibit a more or less polished surface, whereas genuine lard, whether crude or refined, was said to show a fine crystalline texture and a dull wrinkled surface. A differentiation of genuine lard from adulterated lard on the strength of the consistence may have been approximately possible at the time when American hogs were fed on wheat and the lard was hard ; but since fattening with maize and also with cotton seed or cotton seed cake has been resorted to, the consistence has gradually become that of soft butter. It may be pointed out here that some Continental chemists endeavour to differentiate between American and home-rendered (leaf-) lards by the manner in which the melted lard solidifies (" *Wulstprobe*," *Langfurth* [2]).

The following physical and chemical methods are those employed in the detection of adulterants in lard : —

Specific Gravity.—The specific gravity should only be considered as a very rough corroboration of other tests, since some of the usual adulterants have nearly the same specific gravity as pure lard. How-

[1] *Arbeiten a. d. Kaiserl. Gesundheitsamte*, 1907 (xxv.), Heft 2, p. 505   Cp. Fischer and Schellens, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908 (xvi.), 163. Polenske, 1911, i. 30 (*Analyst*, 1911, 497).

[2] Cp. also Soltsien, *Pharm. Zent.*, 1894, 350. E. Seitter (*Zeits. f. Unters. d. Nahrgs-u. Genussm.*, 1908 (xv.), 484) believes that home-rendered (German) lard can be differentiated from American lard by the occurrence of small quantities of soap in the former lard.

ever, as some analysts still attach value to this test it may be stated that cotton seed oil raises the specific gravity, as also does arachis oil. Therefore a sample having a higher specific gravity than 0·861 at 100° C. must be looked upon with suspicion.

The following table contains some specific gravities, reference to which will be found useful :—

Specific Gravity of Lard, Lard Adulterants, and Compound Lards

| Kind of Fat | Specific Gravity at °C. | | | Observer. |
	37·8° (100° F.) (Water 37·8=1)	99° (Water 15·5=1)	100° (Water 40=1)	
Pure Lard .	0·905-0·907	0·860-0·861	0·85997-0·86191	Allen, Pattinson, Crampton
Lard stearine			0·8575-0·85792	Crampton
Cotton seed oil .		0·868·0·8725	0·8672	Pattinson, Allen
,, ,,			0·86681-0·86774	Leone and Longi
Cotton seed stearine	0·911-0·912		0·86463	Allen, Crampton
Beef stearine .		0·8570	0·85444-0·85888	Pattinson, Crampton
Arachis oil .		0·8673		Allen
Cocoa nut oil .	0·910-0·916	0·8736		Moore
Compound lard No. 1			0·86121-0·86222	Crampton
,, No. 2	..	..	0·86289	,,

Fairley and Cooke [1] determined the specific gravities at 50° C. of the following mixtures of lard and cotton seed oil . -

Mixtures of	I Lard, 0·90038 ; Cotton Seed Oil, 0·90879	II Lard, 0·89159 ; Cotton Seed Oil, 0·89092
Lard with 10 per cent of cotton seed oil .	0·90116	0·89216
,, 20 ,, ,, ,, .	0·90209	0·89328
,, 30 ,, ,, ,, .	0·90302	0·89421
,, 50 ,, ,, ,, .	0·90191	0·89617
,, 75 ,, ,, ,, .	0·90736	0·89850

Melting Point.—Although the melting point of a sample is not in itself of great importance (many adulterated lards having the same melting points as pure lard), still its determination should not be omitted. In the case of unadulterated hog's fat it is possible to ascertain from what part of the body the fat has been rendered ; this will be seen by a glance at the following table :—

[1] *Journ. Soc. Chem. Ind.*, 1890, 1162.

*Melting Points of Lards from different parts of Hogs—
North American and European*

Source.	Fat from	Melting Point °C	Observer [1]
American .	Foot (hoof)	35·1	Wiley
	Head	35·5	,.
	Leg	42·5	,,
	Ham	41·5	,,
European	Back	33·8	Spaeth
	Kidney	13·2	,,
	Leaf	41	,,

In the last table, one number only is given for the melting point. It would seem that this melting point only refers to the final point when the lard in the capillary tube has become perfectly transparent. Since, however, lard in the process of melting first commences to soften, then passes through a stage of translucency till it has melted completely to a transparent liquid, and since this process extends over a range of several degrees, the interval should be stated, as is done in the following table [2] :—

Melting Points of Lards (Lewkowitsch)

					Iodine Value.
Lard from the leaf of an English hog [3]		.	41·1-48·9	51·3
Lard from the shoulder	,,	.	33·9-42·8	
Lard from the loin	,,	.	33·9-42·2	
Lard from the back	,,	.	27·2-33·9	
Irish bladder lard	.	.	35·6-46·1	
English bladder lard	.	.	33·9-45	
American lard	.	.	28·9-41·1	
American lard	.	.	33·0-42·0	
American lard	.	.	31·7-43·3	62·3
American lard	.	.	30·0-41·1	

Cp. also table, p. 694.

Goske,[4] taking the solidifying point of lard similarly as is done in the " Titer test," gives the following numbers :—

---

[1] Cp also Dennstedt and Voigtlander's table, p. 701.
[2] Cp. H. Witte, *Zeitschr f. angew. Chem.*, 1913, 10.
[3] English lard rendered by the author in the laboratory.
[4] *Journ. Soc. Chem. Ind*, 1893, 470.

Fat.		Solidifying Point. °C.
Home-rendered lard	European .	27·10-28·62
,, ,,	,, .	26·64-29·34
,, ,,	,, .	29·10-29 95
Pure steam lard .	North American .	24·10-26·00
,, ,, .	,, .	25·05-25·5
, ,, .	,, .	26·40-27·06
,, ,, .	..	24·9
,, ,, .	.. .	23·67-26·18
Adulterated lard .	. . .	30·50
,, ,, .	. . .	29·73-29·80
,, ,, .	. . .	29 90-30·15
,, ,, .	. . .	31·95-33·00
,, ,, .	. . .	35·90-36·58
,, ,, .	. . .	35·50-35·75

The adulterant in the last samples was tallow, the presence of which was masked by the addition of lard oil.

Iodine Value. In the present state of lard manufacture it is not possible to lay down limits within which the iodine values of commercial samples may vary. As the lower limit of the iodine value of European leaf-lard, 46 was given in the second edition of this work. During the last few years, genuine lards rendered in the author's laboratory, from the leaf only, gave values as high as 53·60·44. Yet, the iodine value of the liquid fatty acids of the leaf-lard absorbing 60·44 per cent was 94·11 only. Nor can the upper limit of 63, given in the second edition of this work, be maintained, as recently North American lards of grade (d) have been imported, having iodine values exceeding even 70. A specimen of genuine North American lard examined in the author's laboratory absorbed 76·9 per cent of iodine (iodine value of liquid fatty acids 115·5). Still, a lard, the iodine value of which falls outside the range of 46 to 66, should be looked upon with suspicion, or in the case of lard above 66 as inferior lard (see table, p. 711). It may be here pointed out that the lard from hogs fed on copra shows iodine values ranging from 32·5 to 42·5 (cp. p. 686). The characteristics of such lards are shown in the following table due to *Gibbs and Agcaoili* [1] :—

	Refracto-meter reading at 40° C.	Saponi-fication Value.	Iodine Value (Hanus).	Iodine Value of Fatty Acids.	Melting Point of Fatty Acids, Titre Test.
Maximum . .	47·0	213·7	42·5	46·2	42·3
Minimum . .	44·0	204·6	32·5	36·2	39·4
Mean . . .	45·3	208·9	37·7	41·3	40 4

Of course, the converse does not follow, namely, that a sample with an iodine absorption within the limits named, must be pure, as com-

[1] *Philippine Journ. of Science*, 1910, 33

binations of fats of low (tallow, cocoa nut oil) and high iodine values (cotton seed, arachis, maize oils) enable the adulterator to prepare a variety of mixtures which will satisfy the limits named above. *There-fore a normal iodine absorption cannot be considered in itself as a final proof of purity.* Thus in the case of artificial lards made from steam lard, tallow stearine, and lard oil,[1] to the exclusion of vegetable oils, the iodine value will, as a rule, lie approximately within the above-named limits. The following table, due to *Goske*, gives the iodine values of several artificial lards calculated from those of its components, based on the following iodine numbers :—beef stearine, 20 ; steam lard, 65 ; mutton tallow, 40 ; lard oil, 85.

Fat.	Beef Stearine.	Steam Lard.	Mutton Tallow.	Lard Oil.	Calculated Iodine Value.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent
1	10	90	..	..	60·5
2	15	85	..	..	58 25
3	..	70	30	.	57 50
4	25	45	..	30	59 75
5	35	25	40	..	57·27

The influence of exposure on the iodine value of lard may be gathered from the table, p. 704.

Provided adulteration with foreign fats be excluded, it is possible to ascertain with some measure of accuracy, by means of the ·iodine value, from what part of the animal the lard has been derived. This is shown in the following table :—

[1] In the United States edible lard oil is too valuable to be used for purposes of adulteration.

Source.	Fat from	Iodine Value.	Observer.
North American	Head	85·03	Wiley
		66·2-70·4	v. Raumer
		65·0-66·6	Dennstedt and Voigtlander
		66·0-69·7	Mans
		63	Dupont
	Foot (hoof)	77·28	Wiley
		69·5-69·6	v. Raumer
		68·8	Dennstedt and Voigtländer
		69·4	Mans
		65	Dupont
	Back	63·6-66·7	v. Raumer
		64·7-66·3	Mans
		61·5-65·1	Dennstedt and Voigtlander
		61	Dupont
	Leaf	58	,,
		53·1	Spaeth
		52·55	Wiley
		60·4-66·7	v. Raumer
		59-63	Dennstedt and Voigtländer
		63·3-65·0	Mans
	Ham	67·7-69·0	v. Raumer
		66·6-68·1	Dennstedt and Voigtlander
		68·4-70·4	Mans
	Guts	60	Dupont
South American	Head	59·7	Tortelli and Ruggeri
	Back	56·0	,, ,,
	Paunch	58·2	,, ,,
	Leaf	54·2	,, ,,
European —German	Back	53·0-58·5	v. Raumer
		61·7	,,
	Leaf	50·4	,,
	Ham	55·9	Dennstedt and Voigtlander
Italian	Head	59·2-68	Tortelli and Ruggeri
	Back	60·5-64·4	,, ,,
	Paunch	61-69·0	,, ,,
	Leaf	53·1-57·4	,, ,,

Steam lard, consisting as it does of the mixed fats from all, or from different parts of the animal, may therefore in some cases have a normal value, say up to 63, in other cases it may absorb more iodine, even as much as 76·9 (*Lewkowitsch*).

It will thus be obvious that the iodine value of the **fat** affords but limited information. Nor can the determination of the iodine value of the **liquid fatty** acids, which up to recently *did* furnish *reliable* indications of admixture of vegetable oils and fats be considered as leading to a definite decision regarding the presence of adulterants. Whereas up to about fifteen years ago the rule held good that in the case of European lards, the iodine value of the liquid fatty acids varied between 90 and 96, and in the case of American lards between 95·2

and 106, these limits no longer apply ; for, whilst *Bömer* found in a Westphalian lard, rendered by himself, the iodine value of the liquid fatty acids at 103·5, *Lewkowitsch* found in a North American lard as high a number as 115·5 from " oily hogs."

Even these high figures are exceeded by the iodine values of Chinese and Japanese lards from the back, and of their liquid fatty acids, as will be gathered from the table given on p. 719. Chinese lards have been imported already into Europe (Hamburg), and it appears also that lard from Cochin-China has been shipped to France.

In order to emphasise the importance which the iodine value has in the examination of lard, the author has compiled the following tables :—

| Fat or Oil. | Iodine Value of | | Observer. |
	Fat	Liquid Fatty Acids.	
Lard, " Western Steam Lard " . .	65·4	104·5	Wallenstein and Finck [1]
,, American (18 samples) . .	58·4-62·9	95·2-104·9	Bömer [2]
	..	98-115·5	Lewkowitsch
,, Berlin	52·7	96·6	Wallenstein and Finck
,, Vienna	60·9	95·2	,,
,, Hungarian	60·4	96·2	,,
,, Roumanian .	59·5	96·0	,,
,, Bavarian (5 samples) . .	52·2 61·2	92·8-96·6	v. Raumer [3]
,, Westphalian	52	93·5-103·7	Bömer
,, South American . . .		92·8-100·6	Tortelli and Ruggeri
,, Italian		92-105·3	,,
Beef tallow, Australian . .	38·3	92·2	Wallenstein and Finck
,, Berlin . . .	45·2	92·4	,,
,, Hungarian .	38·6	92·7	,,
Cotton seed oil, American, white .	108·0	117·5	,,
,, ,, ,, yellow	107·8	117·3	,,
,, ,, Egyptian, bleached	106·5	116·8	,,
,, ,, ,, yellow	108·0	118·2	,,
,, ,, Peruvian . .	106·8	147·8	Bömer
,, ,, ...	104·6-105·7	141·9-144·5	Wallenstein and Finck
Niger seed oil	133·5	117·5	,,
Maize oil	122·0	140·7	,,
Arachis oil	98·9	128·5	,,
Rape oil	101·1	120·7	,,
Olive oil	79·3-81·7	96·4-96·7	Bömer
Cocoa nut oil	8·0	54·0	Wallenstein and Finck

[1] *Journ. Soc. Chem. Ind.*, 1894, 79.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1898, 539.

[3] *Zeitschr. f. angew. Chem*, 1897, 210.

| Source. | Fat from | Iodine Value of | | Observer |
		Fat.	Liquid Fatty Acids.	
North American	Head I.	70·0-70·4	102 4	v. Raumer [1]
	„ II.	66·2-66·4	97·8-97·6	„
	„ III.	68 2-68·4	101·2	„
	Back I.	64·6-64·9	101·6-101·0	„
	„ II.	63·6-63·6	102 8-102 3	„
	„ III.	66·5-66 7	100·6-101·1	„
	Leaf I.	66 4-66·7	103 0-102·6	„
	„ II.	62·7-62 9	97·8-97·8	„
	„ III.	60 4-60·7	96·9	„
	Foot	69·5-69 6	98·6-98 3	„
	Ham I.	67·9-67·9	101 6-101·0	„
	„ II.	67·7-67·9	99·9-100 2	„
	„ III.	68 7-69·0	103·0-103·2	„
South American	Head	59 7	100 6	Tortelli and Ruggeri [2]
	Back	56 0	96·4	„ „
	Paunch	58 2	99·1	„ „
	Leaf	54 2	92·8	„ „
Italian	I. Head	68 0	98 2	Tortelli and Ruggeri
	Back	64·4	104·2	„ „
	Paunch	66·6	105·3	„ „
	Leaf	57 2	93·3	„ „
	II. Head	65 9	98·0	„ „
	Back	63 9	98·5	„ „
	Paunch	67 1	99 3	„ „
	III. Head	59 2	95·5	„ „
	Back	60·5	100·6	„ „
	Paunch	61 0	97 9	„ „
	Leaf	53·1	92·0	„ „
	IV. Head	65·6	103·3	„ „
	Back	61 9	102 3	„ „
	Paunch	69·0	101 9	„ „
	Leaf	57·4	94·0	„ „

Owing to the wide variations which the iodine values of the liquid fatty acids exhibit at present, they no longer afford the same certainty in judging a sample of lard as they did some years ago ; we must even expect that the iodine values of genuine lards will slowly move in the direction of the upper limits. Whilst, then, the iodine value of the liquid fatty acids does not afford a definite means of detecting adulteration, still the determination of this value should not be omitted, since it furnishes cumulative evidence in the examination of those samples which must be regarded with suspicion. If the iodine value of the liquid fatty acids of a sample be found much above 110, a presumption is raised that adulteration with vegetable oils—such as cotton seed oil, maize oil—has taken place. On the other hand, if the iodine value of the liquid fatty acids lie much below 90, admixture with cocoa nut oil or palm kernel oil must be assumed.

[1] Zeitschr. f. angew. Chem , 1897, 210.   [2] L'Orosi, 1900, April

It must, however, be repeated that if the iodine value of a sample under examination is found within the permissible limits, the lard cannot yet be pronounced unadulterated. The admixture of a liquid, vegetable oil may have been compensated by the addition of cocoa nut oil or to some smaller extent by beef tallow.

This test must, therefore, be supplemented in doubtful cases by special tests for cocoa nut oil and for tallow (see below).

Thermal Tests.—As a preliminary test, and in cases where a large number of samples must be examined quickly, the rise of temperature on mixing with concentrated sulphuric acid or with bromine may furnish useful results in a short time ; this holds especially good of the second reagent.

Maumené Test.—The rise of temperature which occurs on mixing the sample with sulphuric acid has been recommended for the detection and even for the approximate estimation of cotton seed oil in lard by *Hehner,*[1] *Ambühl, Wiley,* and *Engler and Rupp,* whereas *Williams* failed to obtain decisive results. Since the modern methods of fat analysis have been introduced the examination by the *Maumené* test has become superfluous. In the opinion of the author too much value is ascribed to this test. However, as it is still being used, especially by French analysts, the following notes may be found helpful :—

The numbers obtained by different experimenters vary so considerably, that the safest plan is to make comparative tests with pure specimens of lard and cotton seed oil before examining the sample. It need hardly be mentioned that the sample must be thoroughly dry before testing. The following table contains a few numbers obtained by various observers :—

---

[1] *Analyst,* 13 (1888), 166.

Fat	Rise of Temp. °C.	Method Employed.	Observer.
Lard	24-27·5	50 grms. of fat; 10 c.c. conc H_2SO_4	Hehner
Cotton seed oil	70	"	Ambühl
Lard	13-15	" initial temp. 40° C.	"
Cotton seed oil	50-52	" " "	"
"American" lard	30-35	" " "	Wiley
Lard	41·5	" " 35° C.	"
Cotton seed oil	85·4	" " "	"
Steam lard	38·8-42·1	" " "	"
"Oleostearine"	20·8	" " "	"
Lard stearine	37·7	" " "	"
Artificial lards	42·1-58·9	" " "	"
	51·3-68·8	" " "	"
Lard	31-32	" not stated	Engler and Rupp
Cotton seed oil	81	" "	"
Lard with 10 per cent of cotton seed oil	34	" "	"
" " 20 "	40-42	" "	"
" " 50 "	58	" "[1]	"
Lard	35	" 35° C.	Schweitzer and Lungwitz
Lard oil	45·3	" 45° C.	"
"Oleostearine"	31·9	" 35° C.	"
Cotton seed oil	61·5	" "	"
Compound lard	58·0	" 45° C.	"
Tallow	31·6	" "	"

[1] Acid of 100 per cent H_2SO_4, prepared by mixing fuming acid with conc. commercial acid.

In order to obtain more decisive results the liquid portion prepared by expression may be also examined (*Langfurth*).

Heat of Bromination.—The following numbers were obtained by *Hehner and Mitchell* ;[1] the iodine values calculated from the temperatures observed are collated with those actually found with *Hübl's* solution :—

							I. Heat of Bromination. Rise of Temperature.	II. Iodine Value Experiment.	III. Iodine Value calculated from I
							° C.	Per cent.	Per cent.
Lard No 1	.	.	.	.	.	.	10·6	57·15	58·3
,, 2	.	.	.	.	.	.	10·4	57·13	57·2
,. 3	.	.	.	.	.	.	11·2	63·11	61·6
,, 4	.	.	.	.	.	.	11·2	61·49	61·6
,, 5	.	.	.	.	.	.	11·8	54·69	64·9
,, 6	.	.	.	.	.	.	11·8	63·96	64·9
,, 7	.	.	.	.	.	.	10·2	57·15	56·1
,, 8	.	.	.	.	.	.	10·4	57·80	57·2
,, 9	.	.	.	.	.	.	9·0	50·38	49·5
,, 10	.	.	.	.	.	.	11·0	58·84	60·5
Lard + 10 per cent cotton seed oil					.	.	11·6	64·13	63·8

Refractometric Examination.—The refractometric examination should only be employed as a preliminary test. The numbers recorded in the following tables will then be found useful. It should be noted that the difference between European and American lards is not quite so distinctly shown in the refractometric indications as in the iodine absorption numbers.

Refractive Indices determined by means of the Butyro-refractometer

Kind of Fat.	European		American.	
	Scale Divisions at 40° C.	Observer.	Scale Divisions at 40° C	Observer.
Lard from head .	..	...	52-52 6	Dennstedt and Voigtlander
,, ,, back	50·2-50·4	Mansfeld	51·8-52·4	,,
,, ,, leaf .	51 2	,,	50·2-52	,,
,, ,, outer part of leaf .	50·7	,,		
Lard from belly .	50 4	,,		
,, ,, intestines .	49·0	,,		
,, ,, foot .	..	...	44·8	,,
,, ,, ham .	.	.	51·9-53	,,
,, ,, ,, .	49·1[2]	Bomer	49·7-51·8[3]	Bomer
Beef tallow	49·0	Mansfeld		
Horse fat .	53·7	,,		
Cocoa nut oil .	35·5	,,		
Cotton seed oil .	61	,,		

[1] *Journ. Soc. Chem. Ind.*, 1897, 88.   [2] Liquid Fatty Acids, 42·8-42·2.
[3] Liquid Fatty Acids, 43 1-44·7.

Deviations in the Oleo-refractometer (Amagat and Jean)

Kind of Fat or Oil.	"Degrees" in the Oleo-refractometer.	
	Fat.	Fatty Acids.
Lard	$-12 \cdot 5$	-30
Steam lard	-13	-30
Lard stearine	-10 to -11	
Beef tallow	-16, -17	-40
,, stearine	-34	
Veal tallow	-19	
Cotton seed oil	$+20$	$+10$
,, stearine	$+25$	$+20$
Sesamé oil		-18
Arachis oil	$+5$	
Lard with 10 per cent of beef tallow	-12	
,, ,, 20 ,, ,, ,,	-13	
,, ,, 50 ,, ,, ,,	-11	-33
,, ,, 5 ,, cotton seed oil	-10	
,, ,, 10 ,, ,, ,,	-8	
,, ,, 15 ,, ,, ,,	7	
,, ,, 20 ,, ,, ,,	6	
,, ,, 25 ,, ,, ,,	-5	
,, ,, 30 ,, ,, ,,	-4	
,, ,, 40 ,, ,, ,,	0	
,, ,, 50 ,, ,, ,,	-3	
,, ,, 5 ,, ,, stearine	-11	
,, ,, 10 ,, ,, ,,	-7	
,, ,, 20 ,, ,, ,,	-4	
,, ,, 30 ,, ,, ,,	-3	
,, ,, 40 ,, ,, ,,	-2	
,, ,, 50 ,, ,, ,,	$+1$	
Lard with 20 per cent of arachis oil	-8	-23
,, ,, 20 ,, sesamé ,,	...	-20
,, 40 per cent ; beef tallow 10 per cent , cotton seed oil 20 per cent	..	-24
Steam lard 60 per cent ; beef tallow 15 per cent ; arachis oil 25 per cent	-8	
Lard 60 per cent ; mutton tallow 25 per cent ; arachis oil 15 per cent	-13	-22
Cocoa nut oil	-54	

From the following table, due to *Dupont*,[1] it will be seen that American lards show smaller deviations than European lards ; if judged solely by the standard of European lards, they might be rashly condemned as containing cotton seed oil :—

[1] *Journ. Soc. Chem. Ind.*, 1895, 828.

American Lard.	Oleo-refractometer. Deviation.	Iodine Value.
From leaf . .	− 11·5	58
,, back . .	− 5	61
,, intestines .	− 7	62
,, head . .	− 7	63
,, foot . .	− 4	65
Gut lard . .	− 11	60
Rancid lard . .	− 7	63
,, lard . .	− 6 5	64

The influence of rancidity on the refractometric index is illustrated by the numbers given in the following table ; they are contrasted with the *Reichert-Meissl* values (*Spaeth*) : —

"Degrees" in the Butyro-refracto-meter calculated for 25° C.		Reichert-Meissl Values
After 1 year	After 3 years.	After 3 years.
59·35	62 60	.
60 21	62 30	4·3
60 49	62 45	9·36
57·71	58 75	1 32
60 35	62 70	
61·35	63·10	
58·14	63·1	3·74

The refractive indices rise in the same proportion as do the iodine values. This is, of course, due to the influence of the unsaturated fatty acids (the amount of which is indicated by the iodine value) on the refractive index. This will be gathered from the following table :—

Lard.	Butyro-re-fractometer. "Degrees" at 40° C.	Iodine Value		Solidifying Point C	Melting Point ° C.	Observer.
		Of Fat.	Of Liquid Fatty Acids.			
Chinese Lard .	50·0-53·7	58·1-82·0 [1]				Farnsteiner [2]
Chinese fat from back	53 3-54·4	79-80·8	113·3-121 7			,,
Japanese fat from back	53·8-57·3	80·0-101·7	124·2-138·7			,,
Japanese fat from ham	51·4-55·9	71·5-98·6	111·1-131·5			,,
English lard from :—						
Leaf . . .	48·4	55·9		30·5-32·7		Dunlop
Leaf . . .	48·1	53·0		30·5-31·5	47	,,
Kidney bed . .	48 3	55·3		33·3-33·7		,,
Kidney bed . .	48·2	53·4		33 7-35 0	50	,,
Kidney bed . .	49·2	58·1		27·0-27·8	43	,,
Leg . . .	48·6	57·5		29·0-30·0		,,
Leg . . .	50 0	64·1		21·3-25·5	37	,,
Leg . . .	50·0	65·4		27·6-27·9		,,
Head (cheek) . .	49·4	62 9		26·0-26·7		,,
Back .	49·0	58·4		28·0-28·3		,,
Back . . .	49·7	64·2		26·7-26·8	38	,,
Back . . .	50·7	67·9		25·3	36	,,

The determination and investigation of the **unsaponifiable matter** is of importance in the examination of a suspected lard.

In the early years of lard manufacture on a large scale, adulteration with paraffin wax, up to 20 per cent, had been practised in the United States ; but this mode of adulteration was soon abandoned. During the last few years American lards have been imported containing about 2 per cent of unsaponifiable matter, consisting chiefly of paraffin wax.[3] This may have been introduced into lards adulterated with vegetable fats, in order to defeat the indications furnished by the phytosteryl acetate test. But if this be the only reason, the adulteration would be a very clumsy one, for the added paraffin wax would amount to over 1·5 per cent of the lard, a quantity that can be readily recognised by the appearance of the acetylated unsaponifiable matter when crystallising it from alcohol. A rapid " sorting test " for the detection of paraffin wax in lard is given as follows : 3 c.c. of the melted fat and 10 c.c. of a mixture consisting of equal volume of absolute alcohol and chloroform are heated until a clear solution results and then cooled in cold water. *Thompson and Hurst* [4] state that 1·5 per cent of paraffin wax gave a turbidity within 3 minutes. (As to another likely reason for the large amount of added paraffin wax, see below, " *Wesson's* test.") *Polenske* [5] has shown that quantities falling below 0·1 per cent of paraffin wax (reckoned on lard) are sufficient so to depress the melting point of the acetates in the phytosteryl acetate test that the presence of vegetable fats in a lard would no longer be recognised.[6]

[1] In four specimens, 82·1-85.
[2] *Zeits. f Unters. d. Nahrgs- u. Genussm.*, 1905 (x.), 70.
[3] Olig and Tillmans, *Zeits f Unters d. Nahrgs- u. Genussm* , 1905 (ix.), 597.
[4] *Chem. News,* 1910, 109.
[5] *Arbeiten. a. d. Kaiserl. Gesundheitsamte,* 1905, xxii. 576.
[6] Cp. Vol. i. 584.

Whereas adulteration with vegetable oils and fats can be detected with certainty by the phytosteryl acetate test, the recognition of beef tallow and beef stearine (" oleostearine ") presents considerable difficulties, the more so as small quantities, down to 5 per cent, may repay , the cost entailed in the mixing.

In the following lines special methods for the detection of the more important adulterants are indicated.

Vegetable Oils and Fats

The phospho-molybdic acid test (Vol. I. Chap. VII.) has been recommended by several observers as a method to indicate with certainty the presence of vegetable oils in lard. The author has, however, shown [1] that a slightly rancid lard also reduces the reagent, and, furthermore, that an admixture of less than 15 per cent of cotton seed oil with pure lard cannot be thus detected. This test can therefore only be admitted as a preliminary one. The author's experiments have been repeated and confirmed by other observers (*Samelson and Tennille*).

The surest proof of the presence of vegetable oils is obtained by the phytosteryl acetate test.[2] Even 1-2 per cent of vegetable oils may thus be detected. Since this test is somewhat cumbersome and lengthy in the practice of an analytical chemist, and will therefore only be resorted to when other methods fail to give a decisive answer, the determination of the iodine value of the sample and of its liquid fatty acids should be looked upon as the readiest means of furnishing preliminary information.

If the probable presence of a vegetable oil has been indicated by an abnormally high iodine value, one of the following four oils should be specially looked for :—Arachis oil, sesamé oil, cotton seed oil (cotton seed stearine), maize oil.

Arachis Oil. — This can be approximately calculated from the amount of arachidic acid obtained. It should be emphasised that it is necessary to determine the melting point of the " arachidic acid " ; if it be found to be below 70° C., the precipitate must be recrystallised.[3]

Sesamé Oil.—This would be readily detected by *Baudouin's* reaction. It should, however, be noted that quite recently *Konig and Sehluckebier* [4] demonstrated that on feeding pigs with sesamé cake the substance which gives the *Baudouin* reaction passes into the body fat. This was proved by examining the fat taken from five different parts of the animal (head, back, leaf, ham, intestines) which had served for the experiment.

[1] Lewkowitsch, *Journ. Soc. Chem. Ind* , 1894, 619.
[2] Klamroth, *Inaug. Dissert.*, Munich, 1911.
[3] Cp. W. B. Smith, *Journ. Amer. Chem. Soc.*, 1907, 1756.
[4] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908 (xv.), 648.

Cotton Seed Oil (Stearine). — For the preliminary detection of cotton seed oil or cotton seed stearine in lard the colour reactions described p. 203 may be employed. The most useful amongst these is the *Halphen* test. It has been stated already that an over-estimation of the indications furnished by this test may lead to grave errors. If a positive *Halphen* colour reaction has been obtained, the presumption is raised that the sample of lard is adulterated with cotton seed oil. It must, however, be distinctly understood that no more than a presumption is raised, for a positive test does not indicate with certainty that cotton seed oil is present, nor does a negative test prove its absence. For, as pointed out already, the colouring matter contained in cotton seed passes into the lard from hogs fed on cotton cake. This has been placed beyond doubt by several observers (*Langfurth*,[1] *Soltsien*,[2] *Fulmer*[3]). Hence it would be entirely misleading to conclude from a positive *Halphen* reaction that cotton seed oil is present. More erroneous still would it be to judge from the depth of the tint as to the approximate amount of cotton seed oil present. I lay stress on this, as attempts have been made to convert the *Halphen* test into a colourimetric quantitative reaction. *Langfurth* has shown that lard obtained from a hog fed experimentally on cotton cake gave as strong a colouration as was obtained by a mixture of lard with 30 per cent of cotton seed oil ; he therefore rightly points out that the quantity of lard obtained from a single hog fed on cotton cake would be quite sufficient to contaminate a tank-car of lard, so that the mixture would give a very distinct colouration in the *Halphen* test.

Fulmer has more recently carried out systematic experiments by feeding pigs with cotton seed meal and testing the fat obtained from different parts of the body of the animal. The chromogenetic substance in cotton seed oil passes into all parts of the body, but the intensity of the *Halphen* test was found greater in the fat from the leaf and back than in that from the head. Judged solely by the *Halphen* test, the conclusion might have been derived that some of the lards contained up to 15 per cent of cotton seed oil.

Dunlop[4] confirmed this by examining lards from a pig which had been fed for six weeks with decorticated cotton seed meal (from 1 to 1·5 lb. per day). The numbers in the last column of the following table give the percentages of cotton seed oil that might have been judged to be contained in the lards, if the *Halphen* test alone were taken as the guide.

[1] *Zeitschr. f. angew. Chem.*, 1901, 685.
[2] *Zeitschr. f. offentl. Chem.*, 1901, 140.
[3] *Journ. Amer. Chem Soc.*, 1902, 1148 ; 1904, 837.
[4] *Journ. Soc. Chem. Ind.*, 1906, 458.

Lard from a Pig fed on Cotton Seed Meal

Part of Animal.	Iodine Value.	Butyro-refracto-meter at 40° C. "Degrees."	Cotton Seed Oil, by Halphen's colour test. Per cent.
Shoulder . . .	67·8	50·7	10
Leg . . .	65·1	50·3	8
Back . . .	64·8	50·0	10
Leaf . . .	58·3	49·0	2
Kidney bed . .	58·3	49·0	6

If therefore on examining a specimen of lard, a colouration has been obtained, further tests must be applied, especially the phytosteryl acetate test. Indeed, *Tolman* [1] has shown that the lards obtained by *Fulmer* from pigs fed on cotton seed meal gave normal numbers in the phytosteryl acetate test. In the absence of vegetable fats a positive *Halphen* test would therefore indicate that feeding with cotton seed or cotton seed meal had taken place. If employed with due precaution, the *Halphen* test will be found a very useful preliminary test, especially in those cases where a large number of samples must be examined rapidly. A negative *Halphen* test, as has been pointed out already, does not prove the absence of cotton seed oil, since cotton seed oils which have been heated do not give a colouration with *Halphen's* reagent.

If the *Halphen* reaction gives a negative result, the **nitric acid** test may be usefully applied as a further preliminary one, for, as shown above (p. 204), cotton seed oil after heating still gives a brown colouration. But it must be remembered that lards from hogs fed on cotton cake also give a brown colour. Still, the absence of a brown colouration may indicate the absence of any considerable quantities of cotton seed oil.

The reduction of silver nitrate (by any of the methods described p. 205) by no means proves the presence of cotton seed oil. Lard obtained from hogs fed on cotton cake reduces the *Becchi* reagent strongly. Even lards obtained from normally fed hogs occasionally reduce silver nitrate solution (*Wesson*,[2] *Mariani, Bevan* [3]).

As an example a specimen of lard examined in the author's laboratory gave the following indications :—

Iodine value of lard . . .	76·5
Iodine value of the liquid fatty acids . .	115·5
Unsaponifiable matter	0·35 per cent.

Halphen test; a slight colouration was observed, such as would be indicated by a lard containing an admixture of about 6 per cent of cotton seed oil.

[1] *Journ. Amer. Chem. Soc.*, 1905, 589.
[2] *Journ. Chem. Soc.*, 1894, Abstr. II. 75.   [3] *Analyst*, 1894, 88.

The high iodine value in conjunction with the positive *Halphen* test raised the presumption that this lard was adulterated with cotton seed oil. Hence the examination by the phytosteryl .acetate test became imperative.

A preliminary microscopic examination of the unsaponifiable matter (cp. Vol. I. Chap. IX. (a)) showed that phytosterol was absent, the characteristic crystals of cholesterol only having been observed. The unsaponifiable matter was then examined by the method described (Vol. I. Chap. IX.) with the following result :—

Crystals.						Melting Point. °C.
2nd crop	.	.	.	.	.	. 113
3rd crop	.	.	.	.	.	. 114-114·5
4th crop	.	.	.	.	.	. 115
5th crop	.	.	.	.	.	. 113-114

From these results it became evident that the lard was free from cotton seed oil or any other vegetable oil.

As lard gives a liquid product with **sulphur chloride,** which is soluble in carbon bisulphide, cotton seed oil may also be detected qualitatively by means of that reagent (*B. Warren, Jones* [1]). In the presence of cotton seed oil a hard mass partly insoluble in carbon bisulphide is produced.

The author has tried this method and found it useful as a preliminary test. His observations are given in the following table :—

Mixtures of Lard and Cotton Seed Oil (Lewkowitsch)

5 grms. of fat dissolved in 2 c.c. CS_2, added 2 c.c. S_2Cl_2, and placed on the water-bath

Lard Per cent.	Cotton Seed Oil. Per cent.		Solubility of Product in Carbon Bisulphide.	
100	0	No reaction	Completely soluble	
90	10	Thickens after 35 minutes	,, ,,	
80	20	,, ,, 30 .,	52 per cent ,,	
70	30	,, ,, 26 ,,	39·6 ,, ,,	
60	40	,, ,, 18 ,,	31·8 ,, ,,	
50	50	Solid after 10 ,,	37·4 ,, ,,	
40	60	,, ,, 8 ,,	30·6 ,, ,,	
30	70	,, ,, 7 ,,	32·6 ,, ,,	
20	80	,, ,, 6 ,,	30·0 ,, ,,	
10	90	,, ,, 4 ,,	28·4 ,, ,,	
0	100	,, ,, 3 ,,	24 ,, ,,	

It is advisable to test the sample side by side with pure lard, or better still, with mixtures of lard and cotton seed oil (or cotton seed stearine) prepared in a similar fashion to that illustrated by the table.

[1] *Analyst*, 1888, 170.

Maize Oil.—If arachis and sesamé oils are absent, an abnormally high iodine value can only be due to cotton seed oil or maize oil (with regard to Chinese lard, see above). The solidifying point of the mixed fatty acids would in this case lead to a decision if only one oil be present. If both are present, this method breaks down.[1]

If the iodine value of the lard or of the mixed fatty acids is abnormally low, then the presence of cocoa nut oil or palm kernel oil may be suspected.

Cocoa nut oil or **palm kernel oil** will be recognised by a high saponification value, and especially by a definite *Reichert* value and a notable amount of insoluble volatile acids of the sample.

In order to render the indications of this test still more decisive, the suggestion made by *Mecke*[2] may be adopted, viz. to treat one part of the sample with two parts of 95 per cent alcohol at about 60° C. with frequent shaking. Cocoa nut oil passes into the alcohol to a much greater extent than lard does. After distilling off the alcohol from the alcoholic solution the residual fat is examined, when its saponification value, *Reichert* value, titration number of the insoluble volatile acids (see " Butter Fat "), and also the iodine value will afford important information. *Morrschock*[3] has shown that in case pure lard is tested as described here, the extracted fat is characterised by a considerably higher iodine absorption than that of the original lard.

Experiments carried out by *Arnold*[4] according to the method described p. 699, and detailed in the following table, show the manner in which this procedure may be applied for quantitative purposes :—

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[1] Cp. M'Pherson and W. A. Ruth, *Journ. Amer. Chem. Soc.*, 1907, 921
[2] *Zeitschr. f. offentl. Chem.*, 1904, 9.
[3] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1904 (vii.), 586.
[4] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907 (xiv.) 179.

	Butyro-refracto-meter at 40°C. "Degrees."	Saponi-fication Value.	Reichert-Meissl Value.	Molecular Weight of the Soluble Volatile Acids.	c.c. 1/10 KOH required for Insoluble Volatile Acids (Polenske Method, 5 grms.).	Molecular Weight of the Insoluble Volatile Acids.	c.c. 1/10 KOH required for Insoluble Volatile Acids for 0.5 grms. of Fat (Polenske Apparatus).	Molecular Weight of the Insoluble Volatile Acids.	Iodine Value.	Non-Volatile Fatty Acids — Butyro-refracto-meter at 40°C. "Degrees."	Neutral-isation Value.	Iodine Value.	150 grms. yielded Alcohol-soluble Portion, Grms.
American Lard mixed with 10 per cent of Cocoa Nut Oil													
I. Original Fat	49·8	195·4	0·55	…	0·60	…	0·55	…	62·0	36·4	204·4	62·9	…
II. Alcohol-soluble Fat	51·0	194·3	2·50	136·1	1·25	…	0·85	…	64·4	39·7	203·3	66·5	12
III. Alcohol-insoluble Fat	49·8	196·0	0·55	…	0·55	…	0·50	…	60·4	36·1	204·9	62·7	…
American Lard mixed with 3 per cent of Cocoa Nut Oil													
I. Original Fat	49·6	196·0	1·00	…	0·70	…	…	…	61·1	35·3	203·8	62·1	…
II. Alcohol-soluble Fat	49·3	205·5	4·13	139·2	2·35	…	…	…	60·5	37·0	211·1	64·1	9
III. Alcohol-insoluble Fat	50·0	197·7	0·90	…	0·75	…	…	…	59·9	36·6	205·9	61·3	…
German Lard mixed with 4 per cent of Cocoa Nut Oil													
I. Original Fat	48·9	202·7	1·50	…	0·80	…	…	…	47·1	34·9	210·8	48·6	…
II. Alcohol-soluble Fat	49·1	216·2	5·70	136·7	3·50	194·2	1·70	208·3	45·7	36·2	222·5	49·6	9·9
III. Alcohol-insoluble Fat	49·0	201·6	1·10	…	0·70	…	…	…	46·3	34·2	209·5	49·5	…
German Lard mixed with 4 per cent of Cocoa Nut Oil													
I. Original Fat	49·1	201·1	1·80	…	0·85	191·0	0·65	…	61·7	…	…	…	…
II. Alcohol-soluble Fat	48·7	210·0	5·56	132·0	3·25	…	1·55	…	55·3	…	…	…	9·1
American Lard mixed with 5 per cent of Cocoa Nut Oil													
I. Original Fat	49·2	198·8	1·35	…	0·90	190·0	…	…	60·0	35·0	206·7	62·0	…
II. Alcohol-soluble Fat	49·0	210·6	5·60	142·0	3·95	…	…	…	52·7	36·1	216·4	58·3	9·1
III. Alcohol-insoluble Fat	50·0	197·1	1·00	…	0·75	…	…	…	58·8	…	…	…	…
American Lard mixed with 10 per cent of Cocoa Nut Oil													
I. Original Fat	48·3	202·2	2·37	…	1·30	178·0	…	…	55·4	33·8	209·2	56·2	…
II. Alcohol-soluble Fat	46·9	229·0	8·00	135·3	7·85	…	…	…	39·7	32·0	231·9	42·8	10·2
III. Alcohol-insoluble Fat	49·2	200·0	1·90	…	1·10	…	…	…	55·5	34·0	207·5	56·9	…

In doubtful cases the phytosteryl acetate test—provided other vegetable oils be absent—will furnish conclusive evidence:[1]

Animal Fats

The detection of **tallow** and (or) **beef stearine** in lard is a difficult problem, and can only be solved successfully, in the present state of our knowledge, by strict comparison with samples of pure lards from different parts of the body of hogs, and of the same lards mixed with known proportions of the suspected adulterant. This problem is rendered all the more difficult as lards of different origin vary greatly in their composition, as is shown in the above-given tables.

The first attempts to detect small quantities of beef fat or beef " stearine " in lard were made in the year 1883 by *Belfield* and by *Delafontaine*, both basing themselves on the method published by *Husson* [2] in 1878.

Belfield claimed to be able to detect 10 per cent of beef stearine in lard. He directed to dissolve the sample in ether, and examine under the microscope the crystals which separate from the ethereal solution. Forty drops of the melted lard are dissolved in 10 c.c. of ether in a test-tube and allowed to cool (*Pattinson* [3]). Should no crystals form, the cork is removed from the tube and a loose plug of cotton-wool substituted, when crystals will be obtained by the spontaneous evaporation of the ether. If the crystals have been formed too rapidly it is best to redissolve them by addition of more ether. Some of the crystals are then placed on an object-glass and examined microscopically. Crystals from pure lard usually form oblong plates—either singly or in bunches—and have oblique terminals, whereas those from beef tallow form curved tufts of very thin needles somewhat of the shape of an " *f* " (" plumose " crystals). Cp. Figs. 8, 9, 10.

The author examined microscopically the crystals obtained from specimens of leaf lard, lard from the loin, lard from the shoulder, and lard from the back, all of which were rendered in his laboratory. Forty drops of the melted fat were dissolved in 10 c.c. of ether, and were allowed to crystallise under exactly the same conditions in corked test-tubes.

In the case of *leaf* lard, bunches of crystals were obtained, which under a low power of magnification appeared as needles, but under a higher power were distinctly discernible as plates.

The lard *from the shoulder* yielded some isolated plates, but mostly bunches, radiating from a centre point in all directions, thus forming a whole circle or parts thereof. There also appeared bunches of crystals which were very similar to tallow crystals ; yet under a high power of magnification they showed the chisel-shaped ends characteristic of lard crystals. Small bunches of crystals were, however, noticed which were indistinguishable from beef tallow crystals. Moreover, in various

[1] With regard to Robin's method, cp. *Annal. Chim. Analyt. Appl.*, 1907 (12), 87. Hoton's acetic acid test is referred to in Vol. I. Chap. V.
[2] *Journ. Pharm. Chim.* (4), 27, 100.   [3] *Journ. Soc. Chem. Ind.*, 1889, 30.

preparations the plates did not even predominate over those crystals which appeared to be most like beef crystals.

The lard *from the loin* showed many distinct straight plates with the chisel-shaped ends characteristic of lard crystals. These were even noticeable in the thickest plates which at first, under a low power, appeared like beef crystals. A number of plates were observed, especially amongst those in the bunches, which were curved, and as they had the shape of distinct plates, would appear to represent the transition form of plates to needles.

FIG. 8.—Mutton Tallow Crystals.   50 diam.

The lard *from the back*, which took the longest time to crystallise (no doubt because it was the softest lard), showed distinct plates throughout, both as regards the isolated crystals, as also those heaped in bunches. The plates were much longer than those obtained from any other part. This is most likely due to the time required for crystallisation having been so much longer.

Mixtures of lard from the back-fat with 5 to 10 per cent of tallow, prepared by the author, showed distinct plates of lard crystals side by side with distinct bunches, which, even under a magnification of 670, could not be recognised as having chisel-shaped ends ; these were possibly plates lying on their ends, thus appearing as needles. Still, it would be hazardous to pronounce a definite opinion on the strength of these microscopic indications.

Fig. 9.—Lard Crystals. 50 diam.

Fig. 10.—Beef Tallow Crystals. 50 diam.

Goske [1] stated at first that 5 per cent of beef fat, or 15 per cent of mutton fat (which does not crystallise so well), can be detected if the ethereal solution he allowed to crystallise at a temperature of 12°-13° C. But later he admits that the question becomes complicated if oleomargarine is substituted for beef stearine. Besides, German home-rendered lard did not yield the crystalline plates, crystallising as it did in needles which were not readily distinguishable from those yielded by beef stearine under the same conditions.

From the above observation it follows that examination under a low power of magnification should not be relied upon, but that examination under high powers is distinctly necessary. It should also be noted that if the plates lie on the narrow end, they may appear under the microscope as thin needles, thus leading to the confounding of lard crystals with beef crystals.

The author has further examined crystals obtained from the ethereal solution in *Stock's modus operandi* (see below) from (*a*) leaf lard, (*b*) lard from the shoulder, (*c*) lard from the loin, (*d*) lard from the back, (*e*) various pure American lards, and (*f*) mixtures of all the lards named with 5 per cent and 10 per cent of (1) beef tallow, (2) various brands of " beef stearine," and " oleostearine." All the observations confirm the result already stated, viz. that it would be very hazardous to declare on the strength of the appearance of the crystals under the microscope that adulteration with 5 per cent or 10 per cent of tallow or beef stearine or oleostearine had been practised. In several cases pure lards were judged by the author to contain some adulterant on the strength of the microscopical appearance, whilst some of the adulterated samples were decidedly declared as pure.

The author's conclusion that the microscopic appearance of the " stearine " from samples containing only 5 to 10 per cent of beef stearine must be regarded with the greatest circumspection has found satisfactory confirmation in experiments carried out by *Dunlop*.[2] On recrystallising the " stearine crystals " as obtained in *Stock's* process (see below) from pure beef " stearine " and mutton " stearine," crystals were obtained after the third and fourth crystallisation, which were absolutely indistinguishable from well-formed lard crystals exhibiting the characteristic oblong plates with oblique terminals. In the third crystallisation the fine rods of mutton tallow gave place to thin plates, in many cases with oblique terminals as in lard crystals at a magnification of 380. In the fourth crystallisation the lard form became already more distinct at a magnification of 100, and even of 30 diameters. In the case of beef stearine, the crystals from the first crystallisation closely resembled those of mutton stearine. The second, and especially the third crops of crystals showed a decided change from beef to lard form at a magnification of 380, whilst in the fourth crystallisation the chisel-shaped ends of the plates were clearly seen ; at a magnification of 100 a number of groups were observed which had the appearance of " plumose " aggregates, but the individual crystals resembled lard plates more closely, and not the fine pointed needles of beef crystals

[1] *Journ. Soc. Chem. Ind.*, 1893, 469.   [2] *Ibid.*, 1906, 458.

as seen in the first crystallisation. This will become apparent on
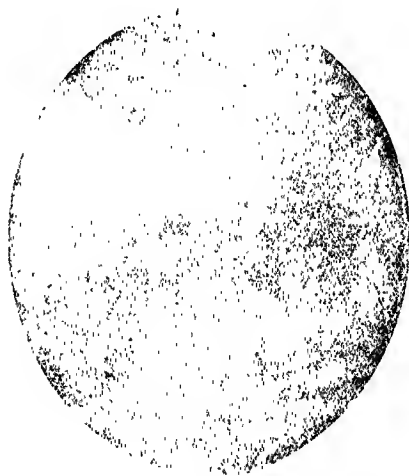
FIG. 11.—Mutton Stearine, 3rd Crystallisation. 380 diam.
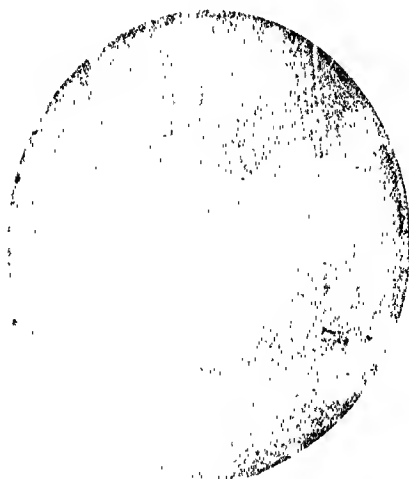
FIG. 12.—Beef Stearine, 3rd Crystallisation. 380 diam.

examining the crystallisations illustrated by Figs. 11, 12, 13, 14 (due
to *Dunlop* [1]). These observations distinctly controvert the statement

[1] *Journ. Soc. Chem. Ind.*, 1906, 458.

made by *Hehner and Mitchell*[1] that crystals from " soft lards " (such

FIG. 13.—Mutton Stearine, 4th Crystallisation.   380 diam.
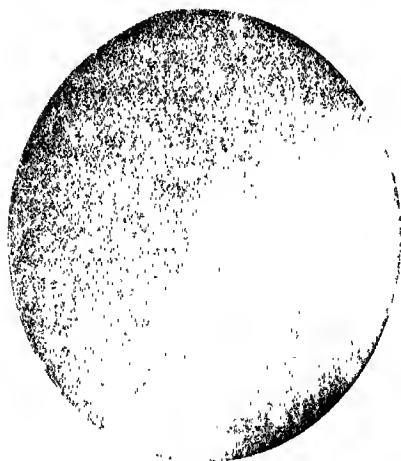
FIG. 14.—Beef Stearine, 4th Crystallisation.   330 diam.

as lard from the back) on being repeatedly recrystallised from ether become more and more needle-like, approaching the form of beef

[1] *Analyst*, 1896, 328.

stearine crystals; until they become indistinguishable from them. A confirmation of this opinion was thought by these observers to be found in the increase of the percentages of stearic acid yielded by crystals obtained from three successive crystallisations of flare lard, they having found the following respective percentages of stearic acid :—32·4 per cent, 37·6 per cent, and 59 per cent. These numbers agree with the results obtained by *Kreis and Hafner* in a similar examination. Their numbers are reproduced in the following table :—

Melting Point. °C.			Iodine Value	Melting Point of the Fatty Acids. °C.	Stearic Acid. Per cent.
Original fat . . .		47·40	58·59	41-42	22·3
	1st Melting Point.	2nd Melting Point			
1st crystallisation	48 0 and	62·0	11·95	56·0	57 5
2nd ,,	50·5 ,,	64 2	1·11	59 5	66·8
3rd ,,	50·8 ,,	64·5	0 21	61 0	67·2
4th ,,	51·4 ,,	65 0	0·13	62 0	67·2
5th ,,	51·8 ,,	65 8	0·14	...	..
6th ,,	51·8 ,,	65·8	0·12	...	...

In conjunction with the last table there should be read the numbers recorded in the following two tables, giving the results of a corresponding examination of beef fat and mutton tallow :—

Beef Tallow

Melting Point. °C.			Iodine Value.	Melting Point of the Fatty Acids. °C	Stearic Acid. Per cent.
Original fat . . .		43-44	35·8	44-45	39·5
	1st Melting Point.	2nd Melting Point.			
1st crystallisation	45·5 and	55·5	9·28	57·5	59·5
2nd ,,	47·0 ,,	58·0	3·28	59·0	64·2
3rd ,,	48·5 ,,	59·0	2 07	60·5	65·5
4th ,,	49·5 ,,	59·8	1·30	62 0	66·4
5th ,,	50 0 ,,	60·0	0·90	..	...
6th ,,	50·0 ,,	60·0	0·86	...	...

[TABLE

Mutton Tallow

Melting Point. °C.			Iodine Value.	Melting Point of the Fatty Acids. °C.	Stearic Acid. Per cent.
Original fat . . .		45	42·5	42·43	35·5
	1st Melting Point	2nd Melting Point			
1st crystallisation	45·5 and	57·5	12·3	58·0	57·8
2nd ,,	47·0 ,,	59·0	6·26	58·8	62·7
3rd ,,	50·5 ,,	60·0	3·41	59·8	65·2
4th ,,	50·5 ,,	60·8	3·00	62·2	67·0
5th ,,	51·0 ,,	61·2	2·70	...	...
6th ,,	51·2 ,,	61·5	2·65	...	...

It has been pointed out already that, in the case of *lard from the loin*, crystals were obtained which would appear to confirm the transition form of plates to needles. *Kreis and Hafner*, who were also unable to confirm *Hehner and Mitchell's* statement, expressed the opinion that the broad plates of lard (Fig. 9) consisted of heptadecyl distearin (" daturodistearin "), whereas hitherto only palmitodistearin and oleopalmitostearin had been obtained from tallow and beef " stearine." Since, however, it has been shown that heptadecylic acid is a mixture of several fatty acids, the more reasonable explanation would be that lard, tallow, and, consequently, beef and mutton stearine yield on repeated recrystallisation from ether one and the same glyceride, which crystallises in those oblong plates with oblique terminals which have hitherto been looked upon as solely characteristic of lard. The author finds a confirmation of his opinion in the following three tables, which have been calculated by *Kreis and Hafner* from the three preceding tables. The iodine values found above are converted into olein. By deducting the numbers so obtained from 100, the percentages given in the column " Olein free Fat " are found. The differences represent glycerides of saturated fatty acids, and the percentages of tristearin therein are calculated from the percentages of stearic acid.

Lard

	Iodine Value.	Olein Per cent.	Stearic Acid.	Tristearin.	Olein-free Fat Per cent.	Tristearin calculated to Olein-free Substance.
			Per cent of Fatty Acids			
Original .	58·59	68·1	22·3	23·3	31·9	73·0
1st cryst. .	11·95	13·9	57·5	60·0	86·1	69·7
2nd ,, .	1·11	1·3	66·8	69·8	98·7	70·8
3rd ,, .	0·21	0·24	67·2	70·2	99·76	70·4
4th ,, .	0·13	0·15	67·2	70·2	99·85	70·3

Beef Tallow

	Iodine Value.	Olein Per cent	Stearic Acid	Tristearin.	Olein-free Fat Per cent.	Tristearin calculated to Olein-free Substance.
			Per cent of Fatty Acids.			
Original .	36·8	41·6	39·5	41·2	58·4	70·5
1st cryst. .	9·28	10·8	59·5	62·1	89·2	69·6
2nd ,, .	3 28	3·8	64·2	67·1	96·2	69·8
3rd ,,	2·07	2·4	65·5	68·4	97·6	70·1
4th ,, .	1·30	1·5	66·4	69·3	98·5	70·3

Mutton Fat

	Iodine Value.	Olein Per cent	Stearic Acid.	Tristearin	Olein-free Fat Per cent.	Tristearin calculated to Olein-free Substance
			Per cent of Fatty Acids			
Original	42 5	49·4	35·5	36·5	50·6	72·1
1st cryst.	12·3	14·3	57·8	60·37	85·7	70·5
2nd ,, .	6·26	7·28	62·7	65·5	92·72	70·6
3rd ,, .	3·41	4·0	65·2	68·1	96·0	70·9
4th ,, .	3·00	3·5	67·0	70·0	96·5	72·5

It will be seen—and this has been pointed out already by *Kreis and Hafner* themselves—that in all three fats the percentages of saturated glycerides calculated to percentages of olein-free glycerides are the same. The increase in the percentage of stearic acid in the successive crystallisations is therefore due to the decrease of olein. It further follows that the difference (if any) between the crystalline form of beef and mutton " stearines " on the one hand, and of lard crystals on the other, cannot be conditioned by a difference in the percentage of stearic acid.

It should, however, be mentioned that *Kreis and Hafner* point out that the last crystallisations from beef fat (sixth and seventh) show distinctly the type of needles. This is at variance with *Dunlop's* observations ; but since *Dunlop's* photomicrographs unmistakably prove his contention, whereas *Kreis and Hafner* have not published photomicrographs of the sixth or seventh crystallisation from beef fat, *Dunlop's* statement should be looked upon as carrying more weight. *Kreis and Hafner's* opinion may be explained by the fact that if the plates lie on their narrow side they may be easily mistaken for needles, although against this it must be pointed out that *Kreis and Hafner* themselves had observed that lard crystals when lying on the narrow side appear like finely curved needles. Further experiments are therefore required to lead to a final decision between the conflicting statements.

Delafontaine's method consisted in dissolving lard in a mixture of alcohol and ether, allowing to stand twenty-four hours at a temperature of 12-15° C., and weighing the crystals which had separated.

Stock[1] combined the methods of *Belfield and Delafontaine,* and worked out more fully the quantitative determination of the " stearine." He compares the crystals obtained from an ethereal solution with those from two standard sets of mixtures; the first consisting of pure lard melting at 34°-35° C., with 5, 10, 15, and 20 per cent of beef stearine melting at 56° C.; the second of pure lard, of melting point 39°-40° C., with 5, 10, 15, and 20 per cent of beef fat melting at 50° C. *Stock* proceeds as follows :—The melting point of the sample is determined first by the capillary tube method. Suppose the melting point be found at 34° C., then 3 c.c. of the melted fat are run into a graduated stoppered cylinder of 25 c.c. capacity ; 21 c.c. of ether, of specific gravity ·720, are added, and the fat dissolved at 20°-25° C. Three c.c. of each of the first set of mixtures are treated in exactly the same way. The five cylinders are cooled down to 13° C., and allowed to remain at that temperature or a lower one—particularly during the last hours—for twenty-four hours.

An approximate estimate as to the amount of the adulterant is arrived at by reading off the apparent volume of deposited crystals. The ether is then poured off as far as possible, and 10 c.c. of fresh ether at 13° C. is added in each case. The contents of the cylinders are well shaken, cooled to 13° C., the proportion of crystals is read off, and the ether poured off as before. The operation is repeated, and the poured-off ether may be used for swilling the deposit out of the cylinders, but no fresh ether must be used. Finally, the contents of the cylinders are emptied into weighed shallow beakers, the ether drained off carefully, the mass allowed, to dry for fifteen minutes at 40° C., and weighed. The weight obtained for the sample under examination is compared with the weight of crystals obtained from whichever of the standards comes nearest to it.

The second set of mixtures is used for samples with a higher melting point.

The actual presence of beef fat should then be proved by microscopical examination, using a 1-inch objective and the C eye-piece.

It may be noted here that the lard from a hog fed on slaughter-pen refuse, which had an iodine value of 40, gave positive indications of beef fat in the *Belfield* test.[2] The iodine value of the liquid acids was 78.

Stock based his deductions as to the presence of beef stearine on experiments made with seven lards only. These were divided by him into two sets, the first embracing lards melting below 39° C., and the second those melting above 39° C. No statement was made as to whether 39° C. defined the point when the lard had melted to a transparent liquid (see above).

Stock's data are reproduced in the following table :—

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[1] *Analyst,* 1894, 2.   [2] Hare, *Journ. Ind. and Eng. Chem.,* 1910, 264.

Melting Point.	Ether-washed Deposit. "Stearine."
°C.	Mgrms.
34	6
34·5	nil.
39	11
41·2	90
42·5	83
45·5	114
45·8	146

Basing himself on these results *Stock* laid down the rule that a lard of a "melting point" below 39° C., and yielding more than 11 mgrms. of "stearine," must be looked upon as adulterated with beef "stearine." The results of examinations made by the author, as also by *Dunlop*, prove that this generalisation is inadmissible. This will be gathered from the following table :—

"Stearine" (Ether-washed Deposit) from 3 c.c. of Lard

	Melting Points. °C.		Mgrms	Observer.
	Commences to melt.	Completely melted.		
Lard from back of English hog	27·2	– 33·9	2·6	Lewkowitsch
Lard from loin ,,	33·9	– 42·8	36	,,
Lard from shoulder ,,	33·9	– 42·8	62	,,
Lard from the leaf ..	38·3	– 47·8	178·2	,,
Pure "Bladder lard," No. 1 .	33·9	– 45	132·2	,,
Pure "Bladder lard," No. 2 .	35·6	– 45·1	136·4	,,
American lard . . .	38·9	– 41·1	38·2	,,
English lard. . . .	30·0	– 41·1	68·2	,,
American lard . . .	33·3	– 41·1	75·4	,,
,, ,, . . .	30·0	– 43·3	70	,,
English lard from back .	36		5	Dunlop
From leg . . .	37		7	,,
From back . . .	38		9	,,
From kidney bed . .	43		49	,,
From leaf . . .	47		115	,,
From kidney bed . .	50		190	,,

Stock even claimed to be able to determine the amount of "beef stearine" present in an adulterated lard by recrystallising repeatedly the "stearine," on the assumption that "lard stearine" is more readily soluble in ether than "beef stearine." The finally obtained "stearine" was then looked upon by him as "beef stearine" and

calculated to the amount of adulterant added. *Dunlop* has, however, shown by exact experiments that the "stearine" from beef fat, obtained by a single crystallisation, is actually more soluble in ether than the "stearine" from the first crystallisation of lard. Any attempt to calculate the amount of "beef stearine" from the recrystallised "stearine" must therefore lead to failure.

Cochran [1] uses fusel oil for the preliminary separation of stearine crystals, which he then examines by the *Belfield-Stock* method. He proceeds as follows :—2 c.c. of the melted fat are placed in a stoppered cylinder graduated for 25 c.c., and 22 c.c. of fusel oil are added. The contents of the cylinder are slightly warmed to effect complete solution, and gradually allowed to cool to 16°-17° C., at which temperature they are kept for two or three hours. The deposited crystals are filtered off, dissolved in ether, allowed to crystallise out as described above, and finally subjected to microscopical examination. *Cochran* claims that smaller proportions of beef fat can thus be detected than by the above-described methods, but it must be open to doubt whether his method yields better results than the one previously described.

In the present state of our knowledge,[2] *Stock's* modification of *Belfield's* method must be considered the best, provided it be used with circumspection such as is indicated by the numbers given in the last and in the following tables : —

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[1] *Journ, Soc. Chem Ind* , 1898, 74.

[2] A curious method to detect and determine the quantity of beef fat in lard was proposed by Balló, viz to measure the amount of air enclosed in the melted fat ; pure lard on solidifying is stated not to enclose any air, whereas pure beef fat encloses air (100 grms. about 6·5-8 8 c c.). Balló is of the opinion that even 3 per cent of beef fat may be thus detected (*Journ. Soc, Chem. Ind* , 1897, 764).

[Table

"Stearine Crystals" obtained from Beef Stearine and Mixtures thereof with Lard by Stock's "Modus Operandi" (Lewkowitsch)

	Melting Point.		Mgrms.
	Commences to melt.	Completely melted.	
	At °C.		
Beef stearine . . .	52·7 –	52·8	1503·0
Leaf lard[1] containing 5 per cent tallow . . .	42·2 –	47·8	171·6
Leaf lard[1] containing 5 per cent beef stearine .	44·4 –	47·2	216
Leaf lard[1] containing 5 per cent oleostearine .	43·3 –	47·2	207
Leaf lard[1] containing 10 per cent tallow . .	31·1 –	48·3	165·6
Leaf lard[1] containing 10 per cent beef stearine .	42·8 –	47·8	260
Leaf lard[1] containing 10 per cent oleostearine .	40·6 –	47·8	278·4
American lard[2] containing 5 per cent beef stearine	30·0 –	46·7	267·4
American lard[2] containing 5 per cent oleostearine	33·9 –	39·1	197·8
American lard[2] containing 10 per cent beef stearine	30·0 –	39·4	189·6
American lard[2] containing 15 per cent beef stearine	.		263·4
American lard[2] containing 20 per cent beef stearine	...		365
American lard[2] containing 30 per cent beef stearine	.		502·8

It will be observed that, curiously enough, the added amount of tallow reduces the quantity of stearine found (an observation which has also been made by *Dunlop*). A lard yielding 178·2 mgrms. of "stearine" gave, after being adulterated with 5 and 10 per cent of tallow, 171·6 and 165·6 mgrms. respectively. In the case of an addition of 5 per cent of tallow to a "hard" lard, neither the amount of stearine, nor the melting point, nor even the microscopic appearance would lead to a safe conclusion.

The examination of the crystals under the microscope should, however, never be omitted.

If a "soft" lard has been adulterated with 10 per cent of oleo-stearine, the indications furnished by the melting point and the amount of stearine, combined with the microscopical appearance, will assist in coming to a conclusion. In such a case the author observed a number

[1] Sample No. 4 of preceding table yielding 178·2 mgrms. of "stearine."
[2] Sample No. 10 of preceding table yielding 70 mgrms. of "stearine."

of aggregates of the "plumose" form which, even under a high power of magnification, were not resolved into plates.

By recrystallising the fats from ether Emery [1] obtained glycerides with the following melting points :—

Fat.	Melting Point. °C.	Fat	Melting Point. °C.
Pure lard	63 8	Lard containing 8% beef fat	61·6
Lard containing 1% beef fat	63 4	,, ,, 9% ,,	61·6
,, ,, 2% ,,	63 2	,, ,, 10% ,,	61·5
,, ,, 3% ,,	63·0	Beef fat	60·6
,, ,, 4% ,,	62·8	Lard	63·6
,, ,, 5% ,,	62 5	Lard and 10% lard stearine	63·8
,, ,, 6% ,,	62·2	,, 15% ,, ,, .	63·6
,, ,, 7% ,,	61·6		

Bomer [2] bases a method for the detection of tallow in lard on the difference values of the mixed glycerides obtained from recrystallising the fats from ether (cp. Vol. 1. 324). In the case of the palmito-distearin obtained from tallow the difference is only 0·1° C., whereas in the case of palmito-distearin from lard the difference is 5·1° C.

The following tables due to Bomer and Limpuch [3] show the difference values for pure tallow and lard and mixtures.

Crystallisations.	Pure Lard.			Pure Beef Tallow.		
	Melting Point. °C.	Soldifying Point. °C.	Difference Value.	Melting Point. °C.	Solidifying Point. °C.	Difference Value.
Original fat	..	..	..	47·5	33 3	14·2
..	45·6	25·2	20·4	53·2	39 5	13·7
1	49·5	29·4	20·1	54·7	41·9	12·8
2	51·9	32 5	19·4	55·8	43·7	12 1
3	55·8	37·6	18·2	57·0	45·0	12 0
4	57·5	39·6	17·9	..	..	..
5	58·6	41 9	16·7	57·9	46·2	11·7
6	62·2	46·3	15·9	58·4	47·0	11·4
7	64·2	48·6	15 6	59·0	47·6	11·4
8	(50·5) 64·7	49·0	15·7	59·8	48·1	11·7
9	(51·0) 65·3	49·4	15·9	(50·2) 60·4	49·0	11·4
10	(51·2) 65·5	49·5	16·0	(51·3) 61·2	49·5	11·7
11	(51·6) 65·8	49·5	16·3 {	(52·6) 62·8-64·9 }	51·0	13·9

[1] U.S. Department of Agric., 1908, Circular 132, 1

[2] Chem. Zeit., 1913, 890.

[3] Zeits f. Unters d Nahrgs- u. Genussm., 1913, 267.

Crystallisa-tions.	Mixture of 90 per cent Lard and 10 per cent Beef Tallow.			Mixture of 80 per cent Lard and 20 per cent Beef Tallow.		
	Melting Point. °C.	Solidify-ing Point. °C.	Difference Value.	Melting Point. °C.	Solidify-ing Point. °C.	Differ-ence Value.
Original fat	46·0	26·8	19·2	45·6	27·2	18·4
1	48·7	29·6	19·1	50·4	33·5	16·9
2	51·0	33·4	17·6	52·3	36·4	15·9
3	55·2	38·8	16·4	54·6	39·3	15·3
4	56·6	40·2	16·4	55·8	..	..
5	57·5	41·8	15·7	56·7	..	..
6	60·8	46·0	14·8	59·6	..	..
7	⌈61·8	47·6	14·2	60·6	..	..
8	(49·7) 62·8	48·5	14·3	61·7	..	..
9	(50·3) 63·3	48·8	14·5	(50·0) 62·0	..	..
10	(50·9) 63·7	49·2	14·5	(50·8) 62·4	..	..
11	(51·4) 64·2	49·5	14·7	(51·4) 62·9	..	..
12	(51·7) 64·9	49·4	15·5	(51·7) 63·6	..	..

Bomer, Limprich, Kronig, and Kuhlmann [1] propose a method for the detection of beef fat in lard on the difference between the melting point of the more insoluble glycerides, and that of the fatty acids prepared from them. Thus glycerides crystallised from lard had a melting point of 68·5° C., and their fatty acids a melting point of 63·3° C., showing a difference of 5·2° C. In some cases the difference amounted to 6·9° C., whereas beef and mutton tallows showed a difference of from 0·1 to 2·6° C. The method is as follows :—50 grms. of the melted fat are dissolved in 50 c.c. of ether and allowed to stand for one hour at 15° C. The crystalline mass is collected on a filter, pressed slightly, re-dissolved in 50 c.c. of ether, and again allowed to stand for one hour at 15° C. Should the melting point of these crystals be below 61° C. they must be recrystallised from ether. A portion of these glycerides is saponified, and the melting point of the separated fatty acids determined. In determining the melting point of the glycerides the crystals should not be previously melted. According to these observers, the presence of beef fat is indicated when with glycerides melting from 60° and 61° C. the observed difference is less than 5·0° C., or with glycerides melting at between 65° and 68·5° C. it is less than 3° C.

Further research is required to solve the problem of detecting with certainty in every case 5 per cent or 10 per cent of beef stearine in lard.[2] The methods which the author suggested in the third edition of this work, viz. the determination of stearic acid and the determination of " daturic acid," are unable to solve the problem satisfactorily in every case.

If by examination of the mixed fatty acids the statement should

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1913 (xxvi.), 559.
[2] Cp. also Soltsien, *Chem. Revue*, 1908, 103 ; Seitter, *Zeits. f. Unters. d. Genussm.*, 1908 (xv.). 485.

be confirmed that lard differs essentially from tallow, in that it contains notable amounts of myristic acid (which is practically absent from tallow), then the fractional distillation of the methylesters might lead to a decision. It should be pointed out that the author has not tested the value of this suggestion by experiments.

In case lard has been adulterated with both beef stearine and a vegetable oil, in other words if a " compound lard " is under examination, then the phytosteryl acetate test alone furnishes the safest information. If it then should be desired to determine the amount of tallow or beef stearine, resort should be had to *Wesson's* cooling test (cp. Vol. III. Chap. XV. " Lard Substitutes ").

In connection with the manufacture of lard there are produced as secondary products—

(a) Lard stearine.
(b) Lard oil.

These two products are manufactured from prime steam lard, by allowing it to crystallise at a carefully regulated temperature, in winter from 45° to 55° F., and in summer from 55° to 65° F., so that the stearine may separate as a crystallised mass, ready to part with the lard oil when subjected to pressure (cp. Vol. III. Chap. XV. " Margarine "). If no proper crystallisation takes place, it is impossible to express the oil, as the whole material passes through the cloths (" spues ") (cp. " Demargarinating process," p. 36). The crystallised mass is wrapped in cloths, in small works by hand, in large works on rotating packing tables. In small establishments lever presses are in use almost exclusively. The lever press is much in vogue for the preparation of a high-class lard oil, where the pressure must be applied slowly. In large establishments automatic, mechanical, or hydraulic presses are employed.

The cakes remaining in the press are sold as lard stearine (French— *Saindoux pressé, Solar stéarine* ; German—*Solar-stearin*).

(a) **Lard stearine** is used in the manufacture of compound lard and—chiefly in Europe—for " stiffening " soft lard. In the United States it is also used in the manufacture of margarine (" oleomargarine ").

Lard stearine from lard unfit for edible purposes is autoclaved and converted into candle material.

The following characteristics have been ascertained for specimens of lard stearine by *Arragon* : [1]—

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[1] *Chem. Zeit.,* 1908, 1227.

[TABLE

	I.	II.	III.	IV.	V.
Specific gravity at 100° C.	0·8585	0·8580	0·8575	0·8578	0·8588
Saponification value	..	195·5	195·5	195·5	194·5
Iodine value . . .	50·7	50·9	48·9	49·6	54·3
Butyro - refractometer "degrees" at 40° C. .	48·5	48·3	47·7	47·5	48·7
Crystals, exhibiting the form of	plates	plates	plates	plates	plates

(b) **Lard oil** (French—*Huile de lard*; German—*Schmalzol*; Italian—*Olio di lardo*), if obtained from the best neutral lard, is used as an ingredient in the manufacture of margarine, etc. Lower qualities are employed as high-class burning and lubricating oils.

According to the pressure and the temperature employed in the process of separating the liquid from the solid portion, the solidifying point of lard oil varies, so that some specimens will deposit " stearine " at the ordinary temperature, or even solidify completely at 10°-12° C., whereas others do not deposit any crystals unless cooled to the freezing point. Hence the usual characteristics, such as the specific gravities, and especially the iodine values of different lard oils, vary considerably, as is evidenced by the numbers contained in the following table :—

[TABLE

Physical and Chemical Characteristics of Lard Oil

Specific Gravity			Saponification Value		Iodine Value		Reichert-Meissl Value		Maumené Test		Butyro-refracto-meter	
At °C.		Observer.	Mgrms KOH.	Observer.	Per cent	Observer.	c.c. N/10 norm KOH	Observer.	°C	Observer.	At 40°C Degrees	Observer.
15	0·916	Duyk[1]	193	Duyk	73	Duyk	0	Duyk	47	Duyk	41	Duyk
15·5	0·915	Allen			67-79[3]	Schweitzer and Lungwitz						
18	0·9137	Long			80·82	Dupont						
20	0·9122	,,			69·7-75·9	Tolman and Munson						
25	0·9088	,,			70-75·2[2]	Vogtlander						
30	0·9053	,,			58[4]	,,						
35	0·9019	,,										
100	0·8626	Duyk										
15·0	0·9155	Lewko-witsch	189·9	Lewko-witsch[4]	86·71	Lewkowitsch	0·21	Lewko-witsch				

Iodine value of the liquid fatty acids, 94·0 to 95·8 in European lard oils; 106 to 109 in American lard oils (*Lewkowitsch*).

[1] *Bull. Assoc. Belge des Chim.*, 1901, 590.   [2] European.
[3] American.   [4] Unsaponifiable matter, 0·88.

Polenske's method may be used for the detection of considerable˙ quantities of tallow in lard, cp. *Fischer and Alpes.*[1]

Tolman and Munson[2] found in a number of lard oils from 18·9 to 26·7 per cent of solid fatty acids by the lead-salt-ether method.

In the elaïdin test lard oil behaves very much like olive oil.

The change which lard oil undergoes on blowing with air at 100° C. is characterised by the numbers given in the following table :[3]—

Blown. Hours.	Specific Gravity.	Refractive Index.	Iodine Value.
0[4]	0·914	1·4697	78·0
3	0·917	1·4699	76·0
6	0·917	1·4700	75·0
9	0·917	1·4705	72·0
12	0·918	1·4707	72·0
15	0·920	1·4708	71·0
18	0·923	1·4709	67·0
21	0·923	1·4710	67·0
24	0·925	1·4713	66·0

Lard oil is a water-white to pale yellow liquid at the ordinary temperature. If made from fresh steam lard it is practically devoid of free fatty acids. Such lard oil is used (chiefly in Europe) in the manufacture of compound lards, and of margarine (" oleomargarine "). Those lard oils which are unsuitable for edible purposes and contain a small amount of free fatty acids are used as high-class lubricating oils, wool oils, finest burning oils, and in the United States in place of olive oil for making silk-scouring soaps, and for lubricating the silk fibre for weaving.

On account of its high price, lard oil is very frequently adulterated, notably so with tallow oil and " greases." Such mixtures exhibit normal numbers in the usual quantitative tests ; their detection is facilitated by organoleptic tests.

Other adulterants, such as mineral oils or vegetable oils, are detected by the quantitative reactions and the methods described above. Fish and blubber oils in lard oil intended for lubricating purposes are best detected by isolating the ether-insoluble bromides of the liquid fatty acids.

BEEF MARROW FAT

French—*Graisse de moelle de bœuf.*   German—*Rindermarkfett.*
Italian—*Grasso di midollo di bove.*

For tables of characteristics see p. 745.

Beef marrow fat is recovered from the marrow bones of cattle. The marrow fat from the shin bones is, in the United States, usually mixed with the oil from the feet (cp. " Neat's Foot Oil ").

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909 (xvii.), 181.
[2] *Journ Amer. Chem. Soc.*, 1903, 966.
[3] Proctor and Holmes, *Journ. Soc. Chem. Ind.*, 1905, 1287.   [4] Original oil.

Physical and Chemical Characteristics of Beef Marrow Fat

Specific Gravity		Solidifying Point.		Melting Point		Saponification Value.		Iodine Value		Reichert Value		Refractive Index Butyro-refracto-meter.	
At 15°C	Observer.	°C	Observer	°C.	Observer	Mgrms KOH	Observer	Per cent	Observer	c.c. N/10 norm. KOH.	Observer.	"Degrees" at 25°C	Observer.
0.9311-0.938	Zink	31-29	Zink	37-45	Zink	199.6, 195.8-198.1	Lewkowitsch, Zink	55.4, 39.2-50.9, 52	Lewkowitsch, Zink, Dunlop [1]	1.1	Zink	55.3	Dunlop

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
At 15°C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms KOH	Observer.	Per cent	Observer.
0.9300-0.9399	Zink	37.9-38.2 [2], 40-39	Lewkowitsch, Zink	45-46.3 [3]	Zink	204.5	Zink	55.5	Lewkowitsch

[1] *Analyst*, 1907, 318.   [2] Titer Test.   [3] Capillary Tube Method

The freshest marrow bones are kept separate from the waste butchers' bones (" streeters "). They are sawn into two and the marrow knocked out.

Medullic acid, stated by *Eylerts* to occur in beef marrow, is, according to *Thümmel*, a mixture of palmitic and stearic acids.

Freshly rendered marrow fat has a low acid value, 0·44 (*Dunlop*[1]), 1·6 (*Zink*). A specimen eight months old gave the number 1·9. Evidently the acid value depends on the state of freshness of the bones. According to *Glikin*,[2] iron seems to occur regularly in beef marrow fat; the marrow of young animals is stated to contain a higher amount of iron than that of old animals.

Nerthing[3] examined separately beef marrow fats from red and yellow marrow. The fat from yellow marrow consisted of 78 per cent of oleic acid, 14·2 per cent of stearic acid, and 7·8 per cent of palmitic acid; and the fat of red marrow of 47·4 per cent of oleic acid, 36·3 per cent of stearic acid, and 16·3 per cent of palmitic acid. The yellow marrow contained 0·3 per cent of cholesterol and 0·18 per cent of lecithin, and the red marrow 0·28 per cent of cholesterol and 0·2 per cent of lecithin.[4]

Beef marrow fat is used in pharmacy and for making pomades.

BONE FAT

French—*Suif d'os*.   German —*Knochenfett*.
Italian—*Grasso d' ossa*.

Bone fat is practically a by-product in the process of working up bones, whether they be intended for the manufacture of char or for the production of glue and gelatine. In either case the " degreasing " of the bones must precede all further manipulations. Bones from heads, ribs, shoulder blades, etc., contain from 12 to 13 per cent of fat, whilst the large thigh bones (" marrows ") contain as much as 18 to 20 per cent. These numbers apply to fresh bones only. The amount of fat that can be recovered decreases according to the age and rancidity of the bones. Bone fat is obtained chiefly by two processes, firstly, by boiling with water at the ordinary pressure or by steaming under high pressure, and secondly, by extracting with volatile solvents.

The oldest process for producing bone fat consisted in boiling the broken bones with water in open vessels and allowing the hot liquor to stand, when the fat separating on the top was skimmed off. If fresh bones were used, the bone fat so recovered had a white to yellowish colour, a faint odour and taste, and possessed the consistence of butter.[5]

[1] *Analyst*, 1907, 318.   [2] *Berichte*, 1908, 910.
[3] *Biochem. Zeits.*, 1908, 167.   [4] *Ibid.*, 1907, 235.
[5] In the United States bone fat of this description is sold under the name "butter-stock-tallow."

If, however, old and putrid bones were employed, the bone fat so recovered passed, according to the age and state of decomposition of the organic matter in the bones, through all gradations, from white fat (containing a few per cent of free fatty acids and an inconsiderable amount of impurities and having a slightly disagreeable smell) to a brownish, less pleasantly smelling fat, and finally to a dark brown mass of offensive odour. This last contained large quantities of free fatty acids, lime soaps (formed by the action of fatty acids on the lime salts of the bones), and, furthermore, calcium salts of lactic acid and of volatile fatty acids (such as butyric, etc.), which are the usual concomitants of rancidity.

By this boiling-out process only half of the fat contained in the bones can be recovered.

Not only was the yield an inferior one, but the nuisance created by the evil smells emitted from bone works has rendered this process a practically obsolete one.

An important improvement in the manufacture consists in treating the bones with steam under pressure. The bones are broken and placed in a cage fixed inside an autoclave, where they are heated with open steam under a pressure of two or three atmospheres. The bone fat resulting from this process is of the same quality as the fat obtained by the obsolete process, especially if the steaming is limited to the shortest possible time, so that only a small amount of glue-yielding material is extracted.[1] In large slaughter-houses, especially those of America (United States and South America), where the bones are worked up in the fresh state, the boiling or steaming out is preceded by a washing operation in " bone - washing machines." These are cylinders usually 10 feet long and 3 feet to 4 feet in diameter, built up from iron bars, 1 inch apart, fixed into two cast-iron heads. They are driven by chain and sprocket and rotate slowly, making about ten revolutions per minute. Through the entire length of the drum there is a hinged door made of bars, which allows the filling and emptying of the cylinder. The machines are usually set at an angle to facilitate the washing and emptying operations. Some manufacturers even resort to steeping the bones in a solution of sulphurous acid in order to obtain a whiter fat (as also a better glue). The yield of bone fat in the steaming-out process under pressure is considerably higher (by about 50 per cent) than in the boiling-out process in open vessels, so that from bones containing 12 per cent of fat, about 8 to 9 per cent can be recovered.

Bone fats of this quality can be bleached, but only the best kinds are likely to yield a good product. The higher the percentage of free fatty acids the greater is the difficulty in bleaching. In fact, products containing more than 50 per cent of free fatty acids could not hitherto be bleached successfully. Bone fats from which the free fatty acids have been removed are much more susceptible to bleaching and deodourising processes than the raw material. In some cases bone fat

[1] H. Hilbert and Bayerische, Aktien-Ges. f. Chem. u. landw. chemische Fabrikate ; French patents 1527 and 1559.

may be bleached with potassium dichromate and hydrochloric acid in the same manner as palm oil is bleached.

Practically the total amount of bone fat in bones can be obtained by treatment with solvents, a process which leaves the animal tissue unimpaired, so that the whole of the glue-yielding organic substances can be converted into glue after the fat has been removed. Hence the *extraction process* has come largely into vogue. Especially those bones which are no longer fresh are worked up in this manner. The solvents used for extraction were up to recently almost exclusively petroleum ether (benzine) and Scotch shale oil (boiling between 212° and 270° F.). Latterly also carbon tetrachloride has been used on an experimental scale. The use of benzol and trichloroethylene has also been advocated in place of benzine. Extraction apparatus may be divided broadly into two classes: 1, those in which the solvent acts on the bones direct; and 2, those in which the vapour is allowed to come into contact with the bones.

The extraction with *benzine* or *shale oil* takes place in iron digesters under pressure, or in open apparatus. The process in which pressure is employed is the more dangerous one, and has not infrequently led to explosions. The yield depends on the time during which the solvent acts on the bones, as also on the construction of the apparatus used. That apparatus will be the best in which the volatile solvent is so successfully condensed that only a small amount is lost. The fat obtained by the extracting process is dark brown, and has a very penetrating, unpleasant smell. This fat contains besides a considerable amount of free fatty acids, lime soaps, calcium lactate, calcium butyrate, hydrocarbons from the petroleum ether, and colouring substances. Hitherto this kind of fat has not been bleached successfully, and even when some immediate improvement was obtained, the colour, as also the unpleasant smell, "reverted" after a short time. *H. Volland* [1] claims to bleach successfully extracted bone fat by means of barium peroxide.

The extraction by means of carbon tetrachloride is carried out in open vessels under ordinary pressure; as the solvent attacks iron, the vessels must be lead-lined. Specimens of carbon tetrachloride-extracted bone fats, which the author has had occasion to examine, were superior as regards smell and colour to benzine-extracted fats (cp. p. 23). This may be ascribed to the fact that carbon tetrachloride permits a lower temperature to be employed; at such lower temperature the organic nitrogenous substances are less attacked than is the case if the higher boiling benzine is used. Hitherto the price of this solvent has militated against its introduction in bone-fat works, and carbon tetrachloride-extracted bone fat has not yet been placed on the market in considerable quantities. For the processes, the original patents must be consulted.[2]

The following statistical data may be of interest :—

[1] German patent 222,669.

[2] V. Girsewald, English patent 13,094, 1911 ; L. Dorner, German patent 218,487 ; E. Berliner, German patent 208,443 ; A. Meiro, English patent 18,468, 1909.

Import of Bones into Germany in Tons during 1902-1911.

Origin.	1902.	1903.	1904.	1905.	1906.	1908.	1909.	1910.	1911.
La Plata . .	1759	3696	253	1250	..	..	..	..	..
Levant . .	2202	1104	1375	1909	710	..	..	..	..
Other countries .	858	783	1079	938	640	..	..	..	..
Total . .	4819	5583	2707	4097	1350	3598	9225	7972	11,839

The following brands are known commercially : " R.K.," " B.W.," and " S.B."

Whereas bone fat obtained by the boiling and steaming-out processes can be used for soap-making, bone fat extracted by means of benzine is utterly unsuitable for that purpose in this country on account of its rank odour, and can only be used in candle works. On the Continent such benzine-extracted fat does find employment in small quantities for inferior soaps. If bone fat intended for soap-making purposes contains a considerable amount of lime, it must first be treated with dilute mineral acid.

Occasionally bone fat is worked up for the preparation of " bone oil " (cp. also " Neat's foot oil "). The process is exactly the same as that employed in the production of tallow oil (see p. 764). " Bone oil " is used as a lubricant, and in the leather industries in a similar manner to neat's foot oil. If practically devoid of free fatty acids, it represents one of the finest lubricating oils on account of its low " cold test."

The chemical composition of bone fat lies between that of marrow fat and tallow. Hence the valuation of bone fat is carried out in a similar manner to that of tallow. But a complication arises through the presence of calcium salts of higher fatty acids, and of calcium lactate and butyrate.

It has been pointed out already (Vol. I. Chap. IV.) that lime soaps tenaciously retain water so that the direct determination of moisture may lead to erroneous results. With regard to impurities of a non-fatty nature, it should be borne in mind that different results are obtained according as the fat is extracted after previous drying (as in the English or German method), or is extracted undried (as in the French method). From dried bone fats most of the lime salts are dissolved by petroleum ether, whereas in the case of undried bone fats most of the soaps remain undissolved. The method employed should, therefore, be distinctly stated when the results of the analysis are returned.

[TABLE

Physical and Chemical Characteristics of Bone Fat [1]

Specific Gravity.		Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.	
At 15·5° C.	Observer.	° C	Observer.	° C.	Observer.	Mgrms. KOH	Observer.	Per cent.	Observer.
0·914-0·916	Allen	15 rising to 17	Schaedler	21-22	Schaedler	190·9	Valenta	46·3-49·6	Wilson
...	...	...	...	...	...	194-195 [1]	Lewkowitsch	48-55·8	Valenta

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value		Neutralisation Value.	
° C	Observer.	° C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.
28 [2]	Hubl	30 [2]	Hubl	57·4 [3]	Morawski and Denski	200	Valenta
...	...	...	...	55·7-57·8 [4]	...		

[1] Prepared by boiling out fresh bones.   [2] Cp. table p. 754.   [3] Crude fat.   [4] Refined fat.

The errors inherent to the older methods are avoided by adopting the process proposed by *Shukoff and Schestakoff* : [1]—

Fatty Matter.—This is determined direct. Weigh off 10 grms. in a small conical flask, add 3 to 5 drops of strong hydrochloric acid, and warm on the water-bath for about one hour, agitating the contents of the flask from time to time, whereby the lime soaps are decomposed. Then add 40 c.c. of petroleum ether, agitate to dissolve the fatty matter, and pour the solution carefully (leaving the few drops of acid at the bottom of the flask) through a tared filter into a second flask ; wash two or three times with petroleum ether, and determine the fatty matter in the ethereal solution as described Vol. I. Chap. IV.[2]

Impurities, organic and inorganic.—The dirt and the acid solution from the first flask are washed with the aid of petroleum ether on to the tared filter, dried, and determined as described Chap. IV. ; of course lime and other inorganic substances are washed away with the acid solution.

Ash.—This is found by incinerating a fresh portion of the sample. The lime of the organic lime salts is thus converted into calcium carbonate ; the amount of the latter may be ascertained by titrating the ash with standardised acid.

Moisture.—This is found by difference (cp. also p. 770).

The fatty matter consists of the neutral fat, of the free fatty acids originally contained in the bone fat, and of fatty acids liberated from the lime salts. It also contains, of course, unsaponifiable matter. Among the latter *Shukoff and Schestakoff* found cholesterol to the extent of from 0·2 to 0·6 per cent. The amount of the unsaponifiable matter is found by the method described in Vol. I. Chap. VI.

The determination of the unsaponifiable matter is of great importance, as during the last few years admixture to bone fat of all kinds of waste fats, especially of those containing considerable amounts of unsaponifiable matter (see Vol. III. Chap. XVI., " Waste Fats "), has been practised in a considerable extent. The examination of the isolated unsaponifiable matter is frequently required, and is carried out by the method given in Vol. I. Chap. IX. Adulteration with wool fat—said to occur in continental bone fats—would thus be readily detected.

The following table reproduces some analyses published by *Shukoff and Schestakoff* : —

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[1] *Chem. Revue*, 1898, 6.
[2] Cp. also Schicht and Halpern, *Chem. Zeit.*, 1907, 279.

Description of Bone Fat	Fatty Matter	Impurities.		Moisture by Difference.	Unsaponi-fiable Matter.	Titer Test.[1]
		Organic.	Inorganic.			
	Per cent.	Per cent		Per cent.	Per cent.	°C.
Russian—Petersburg .	98·65	0·15		1·20	1·80	39·9
,, .	99·00	0·15		0·85	0·82	39·9
,,	99·10	0·10		0·80	0·52	40·2
Russian	99·15	0·10		0·75	0 50	42·5
,, . . .	97·30	0·10	0·40	2·47	1·07	40 3
,, . . .	96 60	0·05	0·50	3·58	1 12	39·1
,, from the South .	94 35	0 25	0·90	4·50	1·40	41·4
,, ,, .	92·45	0·30	0·70	6·55	1·20	40·9
,, ,,	93·35	0 08	0·20	6·37	1·26	39·7
English pale . .	98·20	0·25	0·75	1·42	0·56	39·3
,, "melted stuff"	97·04	0·30	0·15	2·15	...	39·8

The following two tables contain some analyses of bone fats. The first tables is due to *Valenta*,[2] the second to *Troicky*:[3]—

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[1] Cp. table, p. 754.

[2] *Zeitschr. f. Chem. Ind.*, 1887, 265 ; *Journ. Soc. Chem. Ind.*, 1888, 219.

[3] *Chem. Zeit. Rep.*, 1890, 239.

Bone Fat.	No.	Water.	Fatty Acids	Free Fatty Acids.	Melting Point of Fatty Acids	Neutralisation Value. Fatty Acids.	Iodine Value of Fatty Acids.	Ash.	Remarks.
		Per cent.	Per cent.	Per cent.	°C			Per cent.	
Extracted .	1	6·31	89·8	25·8	41·5	206	52·1	1·35	Very impure, nearly black, smell unpleasant.
,, .	2	2·20	93·7	18·7	42·8	204·5	50·9	1·85	Brown.
,, .	3	2·55	91·5	...	41·7	205	51·3	2·01	….
,, .	4	·	·	...	42·0	205	48	·	Fatty acids obtained from No. 1 by distillation.
,, .	5	1·7	93·5	26·5	41·5	200	51·3	1·3	Rather dark.
,, .	6	1·35	·	24·6	41·5	206·1	55·8	0·11	…
,, .	7	...	92·9	18·4	41·8	205·8	52·8	...	Very dark.
,, .	8	...	92·3	20·1	42·0	205		...	…
Boiled out .	9			...	45·1	201	44·3	...	Fatty acids from marrow bones, prepared in laboratory.
,, .	10	·		...	33·5	208·1	75	·	Fatty acids from horse marrow bones, prepared in laboratory.
,, .	11	2·05	90·4	14·8	41·5	207	53·5	...	…
,, .	12	3·08	90·7	21·9	41·7	206	52·8	...	

[1] Cp. table, p. 754.

No.	Description of Bone Fat.	Water.	Ash.	Fatty Acids	Saponification Value.	Iodine Value.	Solidifying Point of Fatty Acids.	Oleic Acid.	Stearic Acid.
		Per cent	Per cent.	Per cent			°C.	Per cent.	Per cent.
1	Boiled out	1·20	0·31	93·20	187·0	57·2	39·0	59·18	31·02
2	,,	0·47	0·94	94·40	194·3	56·0	40·2	58·69	35·71
3	Extracted	0·58	0·56	94·12	193·8	52·0	40·9	54·34	39·78
4	Boiled out, Russian	0·84	2·40	86·10	172·0	50·3	42·65	48·08	38·02
5	Extracted, ,,	0·78	1·25	91·30	188·7	51·5	40·75	52·20	39·10
6	,,	0·85	1·76	91·00	181·0	54·8	40·0	55·86	35·64
7	,,	1·82	1·52	92·40	185·6	55·8	40·1	57·24	35·16
8	,,	0·91	1·06	92·85	187·0	55·2	40·9	56·90	35·95
9	Boiled out, from horse bones	1·52	1·82	91·50	184·0	62·7	36·1	63·69	27·81

For other kinds of bone fat, see Vol. III. Chap. XVI., "Bone Grease."

As has been pointed out already, bone fat is worked up in soap and candle works. It has also been mentioned that the benzine-extracted fat is practically unusable in soap-making. Such bone fat forms suitable material for candle-making purposes. The "stearine" ("stearic acid") obtained from bone fat crystallises readily, but on account of its inferior properties as a candle material bone fat is not worked up by itself (Vol. III. Chap. XV.) for candles, but generally in admixture with other raw materials. The following table gives a distillation of fatty acids from bone fat :—

Fat.	Colour.	Acid Value.	Saponi-fication Value.	Iodine Value.	Titer Test. °C.	Mean Molecular Weight.	Remarks.
Bone fat distillate .	Yellowish	210·2	211·6	43·7	40·4	286·1	Average sample
,, 1st fraction	White	220·0	220 0	41·7	40·3	255·3	Amorphous
,, 2nd fraction	Yellowish	211·4	211 4	52·3	41·0	265 6	Crystalline
,, 3rd fraction	Yellow	197 5	198 0	59·2	41·9	284·3	Amorphous

The impurities contained in bone fat, notably the fatty acids of low molecular weight, pass into the glycerin waters. They are liable to ferment, and the crude glycerin finally obtained contains impurities which are not readily removable even by distillation. Dynamite glycerin made from such raw material not infrequently contains tri-methyleneglycol (see Vol. III. Chap. XV.).

TALLOW [BEEF TALLOW, MUTTON TALLOW]

French—*Suif* (*de bœuf, de mouton*). German—*Talg* (*Rindstalg, Ham-meltalg*). Italian—*Sego* (*di bove, di montone*).

In commerce a distinction is made between *beef tallow* and *mutton tallow*. The former is obtained from oxen, cows, and calves; the latter from sheep and goats. This distinction is, boardly speaking, supported by chemical differences in the composition of the respective triglycerides, mutton tallow being as a rule richer in stearin than beef tallow (see below).

Mutton tallow has a stronger and more unpleasant flavour "animal flavour" than beef tallow, which inhibits its use as an edible fat in the margarine industry.

The quality—especially the hardness—of tallow depends on the breed and the age of the animal, and to some extent on the food.[1] The fat from the male beast is generally harder than that obtained

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[1] Cp. Moulton and Trowbridge, *Journ. Ind. and Eng. Chem.*, 1909, 761.

from the female. Animals fed on grass yield a harder fat than those fed with oilcakes; brewery refuse produces especially soft tallow. Hence we have all gradations, from the hard South American beef tallow to home-melt tallow of somewhat softish consistence.

The rough fat is delivered with the adhering tissue, etc., to the tallow-melters, and is rendered at a temperature of about 100° C. or above, as has been described already, p. 3.

The fats from different parts of the carcass, although of unequal value, are not kept separate, unless the fat be intended for the manufacture of oleomargarine, or of best commercial quality.

At present the tendency prevails to collect the rough fat as far as possible in large rendering establishments fitted up with modern appliances. Hence the slaughter-houses in large towns—especially on the Continent—have at present as an adjunct a tallow-rendering establishment. These are found on the most gigantic scale in the large packing-houses of the United States of America as also of South America.

For the production of tallow for the manufacture of margarine the more valuable kidney fat (" suet," " edible fat ") and bowel fat (" midgerum fat ") [French, *suif en branches* or *en rames*; German, *Rohkern*] is dealt with separately and not mixed with the caul- (or kell-, i.e. *omentum*) fat and the fat from other parts of the carcass [French, *dégraisse*; German, *Rohausschnitt*].

By melting this selected fat at low temperatures—not exceeding 50° C.—the " premier jus " is obtained (cp. Vol. III. " Margarine ").

The production of " premier jus " and the further working up of the same into " beef stearine " (or " mutton stearine ") and oleo-margarine, " oleo oil," is carried out on practically the same lines as described under the heading " Lard." Fuller details are given in Vol. III. under the heading " Margarine." The best suet is known as edible tallow.

The following commercial brands of tallow are differentiated :—

(1) Rendered tallow, which contains all the fat from the carcass.

(2) " Premier jus."

(3) Pressed tallow (tallow stearine, beef stearine, mutton stearine, oleostearine).

(4) Oleomargarine, oleo oil.

The first-named quality of tallow, viz. " rendered tallow," is frequently expressed in hydraulic presses for the preparation of tallow stearine and tallow oil (see below).

It is almost impossible to estimate the quantity of home-melt tallow produced in European countries, as the production is scattered over the smallest establishments embracing even those of butchers in villages. The amount of home-melt tallow produced depends, of course, on the stock of cattle and sheep kept in each country. From carefully collected private information the author estimated that the production of home-melt tallow of the United Kingdom in 1900 represented a value of £3,000,000 corresponding to over 100,000 tons. This seems to have increased in the year 1902 by about 10 per cent. But no absolute

reliance can be placed on these figures, and it would rather appear from official publications that the amount is decreasing, for whilst the number of cattle kept in this country in 1871 amounted to 9,320,000 heads, and had increased to 11,504,000 in 1900, the number of sheep had actually decreased from 33,192,000 heads in 1871 to 29,746,000 in 1900. This is further confirmed by the following numbers taken from the " Agricultural Returns of Great Britain " :—

	England.	Wales.	Scotland.	Total for Great Britain.
Cattle—	Heads.	Heads.	Heads.	Heads.
1906	5,060,862	747,715	1,202,279	7,010,856
1907	4,988,183	738,884	1,185,452	6,912,519
1908	..	..	..	6,905,134
1909	..	..	..	7,020,982
1910	..	..	..	7,037,327
1911	..	..	..	7,114,264
Sheep—				
1906	14,839,927	3,586,095	6,994,338	25,420,360
1907	15,099,976	3,703,372	7,313,155	26,116,503
1908	..	..	..	27,119,730
1909	..	..	..	27,618,419
1910	..	..	..	27,102,945
1911	..	..	..	26,494,992
Pigs—				
1906	1,983,602	209,660	130,199	2,323,461
1907	2,257,178	232,996	146,634	2,636,808
1908	..	..	..	2,823,482
1909	..	..	..	2,380,887
1910	..	..	..	2,349,946
1911	..	..	..	2,822,154

An approximate estimate as to the amount of " home-melt " tallow that is obtained from imported living animals may be derived from the numbers reproduced in the following table :—

Heads of Imported Living Animals

	Oxen and Bulls.	Cows.	Calves.	Sheep and Lambs.
1903	518,435	1,411	..	348,660
1904	545,005	1,138	..	374,098
1905	560,202	796	80	174,706
1906	555,544	..	1	90,643
1907	463,047	3,687	143	95,534
1908	378,566	4,254	309	78,900
1909	310,438	10,507	395	8,131
1910	201,969	17,263	329	427
1911	188,594	11,410	394	47,673
1912	44,790	3,839	283	15,430

Corresponding returns for other countries, as far as they are available, are collated in the following table :—

	Cattle.		Sheep.	
	Year.	Heads.	Year.	Heads.
France	1893	12,879,000	1862	29,500,000
	1904	14,137,000	1882	23,800,000
	1905	14,315,552	1900	20,180,000
	1907	13,949,722	1904	1,780,000
	1908	14,239,730	1905	17,783,209
	1909	14,297,570	1907	17,460,284
	1910	14,532,030	1908	17,456,380
	1911	14,552,430	1909	17,357,640 *
	..	..	1910	17,110,760
	..	..	1911	16,425,330
Germany	1873	15,777,000	1873	25,000,000
	1883	15,787,000	1883	19,190,000
	1900	18,391,000	1892	13,590,000
	1904	18,940,000	1900	10,865,000
	1907	20,630,544	1904	9,690,000
	1908	..	1907	7,703,710
	1909	..	1908	..
	1910	..	1909	..
	..	..	1910	..
Austria	1891	8,644,000	1868	5,025,000
	1900	9,511,000	1880	3,841,000
	1902	9,025,257	1901–4	2,621,000
	1910	9,160,009	1910	2,428,101
Hungary	1884	4,879,000	1870	15,076,000
	1895	6,738,000	1880	9,389,000
	1906	6,511,362	1901–4	8,122,000
	1907	6,806,781	1906	7,581,287
	1908	7,336,764	1907	8,113,907
	1909	7,152,568	1908	8,460,375
	1911	7,318,088	1909	7,904,634
	..	..	1911	8,547,042
Russia	1883 [1]	46,725,000	1870 [1]	45,297,000
	1900	43,587,000	1882 [1]	47,509,000
	1904	33,710,000	1901–3	70,647,000
	1905	33,773,335	1904	53,185,000
	1906	31,994,849	1905	44,236,101 [2]
	1707	31,169,356	1906	41,513,110 [2]
	1908	30,800,826	1907	38,036,396 [2]
	1909	31,472,878	1908	38,048,736 [2]
	1910	31,300,345	1909	40,149,326 [2]
	..	..	1910	38,469,432 [1]

[1] The provinces of the North Caucasus are not included.
[2] Including goats.

	Cattle.		Sheep.	
	Year.	Heads.	Year.	Heads.
Algeria	1870	725,000	1870	4,919,000
	1881	1,112,000	1881	5,995,000
	1890	1,233,000	1890	8,952,000
	1900	992,000	1900	6,723,000
	1904	1,080,000	1904	8,611,000
	1905	1,066,404	1905	9,062,036
	1906	1,078,218	1906	8,799,730
	1907	1,081,734	1907	9,314,515
	1908	1,092,202	1908	9,632,177
	1909	1,100,586	1909	9,066,916
	1910	1,127,577	1910	9,042,302
	1911	1,113,952	1911	8,528,610
United States of America .	1890	52,802,000	1890	43,431,000
	1900	43,902,000	1900	41,883,000
	1904	61,242,000	1904	45,870,000
	1906	66,861,522	1906	50,631,619
	1907	72,533,996	1907	53,240,282
	1908	71,267,000	1908	54,631,000
	1909	71,099,000	1909	56,084,000
	1910	69,080,000	1910	57,216,000

None of the European countries are at present exporting tallow, the quantities exported from the United Kingdom being in fact re-exports. Russia, which up to about two decades ago was a tallow-exporting country, has been forced to draw upon the world's supply for her own demands. Indeed the production in Russia is rapidly decreasing. The United States has also ceased to export tallow and now imports from South America.

The chief sources of tallow—in addition to the "home-melt" production—are at present Australasia, South America,[1] and North America. The quantities imported into the United Kingdom and the surplus exported to the Continent of Europe are given in the following table :—

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[1] The export from the Falkland Islands in 1912 was 180 tons.

Imports of Tallow into, and Exports from, the United Kingdom

Import of Tallow.	1897.	1898.	1899.	1900.	1901.	1902.	1903.	1904.	1905.	1906.	1907.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
From Argentine Republic .	5,381	8,202	6,328	8,914	10,229	21,842	14,293	18,295	18,040	11,371	16,059
" United States[1] .	13,577	28,593	27,860	28,531	20,197	9,108	15,037	18,605	18,186	22,985	24,180
" Australasia[2] .	69,695	53,006	58,196	60,811	49,255	43,076	29,437	39,694	45,523	52,776	52,033
" other countries .	8,586	11,289	10,669	10,636	9,589	15,084	10,992	11,310	9,347	9,558	12,735
Total .	97,549	101,096	103,057	108,900	89,261	88,105	69,759	87,904	91,096	96,590	105,007
Exports of Tallow .	49,768	52,191	49,122	46,339	47,478	38,063	34,221	43,330	45,416	59,268	53,140

1 These figures include "greases."　　2 Australasia includes New Zealand.

More detailed figures for the years subsequent to 1907 are given below :—

Imports of Tallow, Unrefined, and Stearine

	1908.	1909.	1910.	1911.	1912.	1913.
	Cwts.	Cwts.	Cwts.	Cwts.	Cwts.	Cwts.
Germany	9,322	10,523	12,281	14,181	12,552	..
Netherlands	9,400	11,019	21,213	18,469	5,838	..
Belgium	55,623	54,203	50,340	52,062	44,320	..
France	36,605	40,134	43,756	31,056	26,175	..
China (exclusive of Hong-Kong, Macïo, and Wei-hai-Wei)	56,038	119,064	74,266	21,716	94,316	..
United States of America	427,915	263,385	48,089	140,824	81,539	92,120
Uruguay	73,209	50,059	173,829	51,464	88,124	..
Argentine Republic	447,498	429,637	412,628	437,519	491,118	240,540
Other foreign countries	8,426	8,366	17,148	12,308	13,422	159,860
Total from foreign countries	1,124,036	986,390	853,550	780,499	857,404	..
British East Indies	4,620	1,883	892	20	..	..
Australia	542,279	735,988	1,099,514	998,231	828,585	} 1,329,540
New Zealand	377,007	459,525	499,204	413,305	438,528	
Canada	1,871	1,740	538	3,010	..	..
Falkland Islands	6,068	10,164	7,296	7,027	..	..
Other British Possessions	836	866	1,777	1,572	11,955	137,620
Total from British Possessions	932,681	1,210,166	1,609,221	1,423,185	1,279,068	..
Total	2,056,717	2,196,556	2,462,771	2,203,664	2,136,472	..
Exports of Tallow	1,014,525	1,068,778	1,295,752	1,173,769	977,956	..

As a complement to the above table the author gives in tabular form the shipments of Australian tallow to Europe : —

Australian Shipments to Europe

Year.	Tons.	Year.	Tons.
1895	76,650	1905	38,300
1896	48,250	1906	43,100
1897	51,600	1907	42,600
1898	45,000	1908	38,900
1899	46,143	1909	55,800
1900	47,000	1910	72,300
1901	40,000	1911	69,000
1902	32,400	1912	58,500
1903	25,900	1913	72,200
1904	35,400		

The amount of beef tallow exported from the United States in lbs. and its value in dollars is given in the following table :—

Fiscal Year.	Lbs.	Dollars.
1896	52,759,212	2,323,674
1897	75,108,834	2,782,595
1898	81,744,809	3,141,653
1899	107,361,009	4,367,356
1900	89,030,943	4,398,204
1901	77,166,889	3,848,561
1902	34,065,758	1,924,577
1903	27,368,924	1,623,852
1904	76,924,174	3,801,302
1905	63,536,992	3,022,173
1906	97,567,156	4,791,025
1907	127,857,739	7,182,688
1908	91,397,507	5,399,219
1909	53,332,767	3,000,366
1910	29,379,992	1,779,615
1911	29,813,154	1,933,681
1912	39,451,419	2,388,046

The amount of tallow imported into the United States is given in the following table :—

Imports

Fiscal Year.	Lbs.	Value in Dollars.
1904	104,767	11,662
1905	278,188	16,887
1906	908,259	63,805
1907	424,876	29,925
1908	304,765	23,074
1909	364,964	25,299
1910	911,472	68,483
1911	984,383	81,640
1912	347,837	25,595

The imported tallows are chiefly of the first-named quality, viz. rendered tallow containing all the fat from the carcass. These tallows are sold according to their *titer* (*titre*) and *colour*. A description of the titer test has been given Vol. I. Chap. VIII., where also its commercial importance has been discussed, and titer test values of the commercial tallows have been tabulated.

As regards colour, the commercial brands are differentiated as " good colour," " off colour," " no colour," etc., and are merely judged by the standards agreed upon between sellers and buyers on the London market. There is a further distinction made between " beef," " mutton," and " mixed " tallows.

During recent years, in consequence of the great demand for edible

fats, the production of " premier jus " for export to Europe has been
established on a large scale in oversea countries. Such tallow is not
only carefully prepared from selected rough fat (see above), but it is also
filtered over fuller's earth, so that it arrives in a perfectly sound state
in Europe, and when carefully packed will keep for months in a sound
condition. Thus the production of oleomargarine and oleostearine for
export to Europe has assumed considerable dimensions during the last
few years. It may be noted here that tallow gives on an average 60
per cent of oleomargarine and 40 per cent of pressed tallow.

The exports of oleomargarine (oleo oil), including neutral lard, from
the United States in lbs. and their value in dollars are given in the
following table :—

Fiscal Year.	Lbs.	Dollars.
1896	103,276,756	8,087,905
1897	113,506,152	6,742,061
1898	132,579,277	7,904,413
1899	142,390,492	9,183,659
1900	146,739,681	10,503,856
1901	161,651,413	11,846,373
1902	138,546,088	12,254,969
1903	126,010,339	11,981,888
1904	165,183,839	12,873,558
1905	145,228,215	11,485,145
1906	209,658,075	17,445,976
1907	...	16,819,933
1908	215,479,332	19,578,222
1909	182,874,304	19,420,376
1910	129,510,307	14,655,052
1911	180,358,657	18,201,515
1912	192,412,458	20,461,591

The dimensions which the trade in oleomargarine has assumed
may be gathered from the following tables :—

Imports of Oleomargarine into the United Kingdom

	Value.		Value.
	£		£
1898	257,595	1905	495,212
1899	263,435	1906	591,058
1900	300,253	1908	1,226,722
1901	298,810	1909	1,284,554
1902	292,988	1910	1,116,383
1903	370,000	1911	739,974
1904	324,115	1912	834,282

Exports of Oleomargarine from the United Kingdom

	Value.	
	Exports of Home Production.	Re-exports of Imports.
	£	£
1898	21,954	56,410
1899	26,874	53,076
1900	16,803	87,834
1901	16,857	83,438
1902	31,283·	60,566
1903	10,048	81,082
1904	3,309	80,347
1905	10,730	188,731
1906	21,733	205,363
1908	30,187	261,335
1909	80,226	358,881
1910	206,360	467,008
1911	351,496	306,743
1912	437,873	455,821

On pressing tallow for the production of " stearine " tallow oil is obtained as a by-product.

Tallow oil (French, *huile de suif*; German, *Talgol*) is liquid or semi-solid according to the temperature at which it has been expressed. Tallow oil is chiefly used in admixture with mineral oils as a lubricating oil. Its solidifying and melting points, as also its iodine values, naturally vary according to the conditions under which the tallow has been expressed. Hence the following characteristics have only limited application [1] :—

Specific Gravity. at 100° C.	Titer Test. ° C.	Iodine Value.	Iodine Value Mixed Fatty Acids.	Maumené Test. ° C.
0·794	34·5-37·5	55·8-56·7	54·6-57	35·0

BEEF TALLOW

French—*Suif de bœuf*.   German—*Rindertalg*.
Italian—*Sego di bove*.

For table of characteristics see p. 768.

Beef tallow when freshly rendered is nearly white, free from disagreeable odour, and almost tasteless. Such quality is represented

[1] Gill and Rowe, *Journ. Amer. Chem. Soc.*, 1902, xxiv. 466.

by " Home-melt beef tallow." Imported tallow passes through all gradations, from " bleached " white to slightly yellowish tallow (Australian), through darker yellow (North American, South American) to finally the off-coloured lowest grades (North American, Australian " no colour ").

Tallow was until recently considered to consist exclusively of the glycerides of palmitic, stearic, and oleic acids. The amount of olein used to be calculated from the iodine value. Thus a tallow absorbing 43 per cent of iodine was looked upon as containing 50 per cent of olein. It is not unlikely that owing to the influence of vegetable fats given with the food (oileakes, etc.) less saturated acids than oleic acid may be found. *Farnsteiner* claims to have obtained small quantities of linolenic hexabromide, pointing to the presence of small quantities of linolenic acid in beef tallow.[1] Recent researches have further shown that it is no longer permissible to adopt the view that palmitin, stearin, and olein are contained as simple triglycerides in tallow, as the following mixed glycerides (although still in an impure state) have been isolated by crystallising tallow from solvents :—oleodipalmitin, stearodipalmitin, oleopalmitostearin, palmitodistearin (see Vol. 1. Chaps. I. and XII.).

Recently *Börner* [2] has shown that by frequently repeated crystallisation of tallow from ether approximately $1\frac{1}{2}$ per cent of pure tristearin can be isolated.

The examination of tallow by the fractional distillation of the methylesters of its mixed fatty acids for the presence of small quantities of myristic acid is desirable (cp. " Lard," p. 698).

On treating beef fat and oleomargarine with 95 per cent alcohol in the same manner as described under " Lard " (p. 699), glycerides richer in olein pass into the alcoholic solution. The characteristics (1) of the original fat, (2) of the alcohol soluble, (3) of the alcohol insoluble portion are collated in the following table (*Arnold* [3]) :—

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1899, 25.
[2] *Ibid.*, 1907 (xiv.), 196.
[3] *Ibid.*, 1907, 179.

	Butyro-refracto-meter at 40° C. "Degrees."	Saponification Value.	Reichert-Meissl Value.	c.c. N/10 KOH required for Insoluble Volatile Acids (Polenske's method).	Iodine Value.	Non-volatile Fatty Acids — Butyro-refracto-meter at 40° C. "Degrees."	Non-volatile Fatty Acids — Neutralisation Value.	Non-volatile Fatty Acids — Iodine Value.	150 Grms. yielded Alcohol-soluble Portion. Grms.
Beef Fat									
I. Original Fat	46·3	199·6	0·80	0·55	42·9	32·6	207·2	45·9	...
II. Alcohol-soluble Fat	47·2	196·0	0·88	0·70	54·0	36·7	203·7	55·9	6·8
III. Alcohol-insoluble Fat	46·4	200·5	0·61	0·60	42·1	32·0	207·8	43·9	...
Beef Fat									
I. Original Fat	46·2	199·1	0·61	0·60	37·5	32·9	206·8	38·3	...
II. Alcohol-soluble Fat	50·2	193·9	0·94	0·80	55·5	38·1	203·0	57·5	5·0
III. Alcohol-insoluble Fat	46·0	200·5	0·55	0·55	36·2	32·4	207·9	37·4	...
Oleomargarine									
I. Original Fat	47·4	199·4	0·66	0·55	46·3	33·2	208·3	48·1	...
II. Alcohol-soluble Fat	49·7	198·2	2·00	0·75	51·8	38·5	205·9	55·1	6·6
III. Alcohol-insoluble Fat	47·5	200·0	0·55	0·60	46·3	33·1	207·6	47·9	...
Oleomargarine									
I. Original Fat	47·45	199·4	0·80	0·50	48·8	...	...	...	...
II. Alcohol-soluble Fat	48·6	193·6	1·30	0·75	54·4	...	...	...	...
III. Alcohol-insoluble Fat	47·3	199·8	0·70	0·55	48·5	...	...	...	...

The proportions of palmitin, stearin, and olein in the fats rendered from different parts of the same beast vary.

The following table compiled from the figures published by *Moulton and Trowbridge* [1] shows the characteristics of fats from different parts of

[1] *Journ. Ind. and Eng. Chem.* 1909, 761.

the beast. The samples were taken from nine steers. These observers conclude that the iodine value of the fat increases with the age of the animal and also with the fatness. The internal fats have lower iodine values than those near the skin.

	Iodine Value.		Melting Point.		Saponification Value.	
	Max.	Min.	Max.	Min.	Max.	Min.
Kidney fat . . .	40·84	29·50	48·10	45·05	199·9	192·3
Offal fat . .	38·39	30·60	48·58	45·30	199·1	195·8
Circulatory system .	31·78	31·17	48·10	45·95	201·7	196·1
Loin fat . . .	43·64	32·30	46·75	41·95	200·4	189·4
Head-tail fat . .	42·38	35·35	45·20	43·50	..	..
Inside chuck fat .	46·90	34·04	46·05	40·50	199·3	195·5
Cod fat . .	46·91	36·57	45·25	39 85	199·5	196·9
Chuck-neck fat . .	45·05	39·93	44·70	41·50	195·1	..
Rib fat . . .	47·14	36·32	46·55	39·80	200·4	185·2
Composite fat . .	45·90	36·74	44·70	42·00	197·0	..
Fat between hind legs	44·83	41·51	42·80	39·65	201·1	..
Flank fat . . .	47·36	43·68	44·90	41·70	194·0	184·8
Rump fat . .	47·55	37·13	44·65	39·60	197·8	194·30
Round fat·. . .	49 25	37·13				
Plate fat . . .	49 44	47·11	42·70	40·70	196·0	..
Shin-shank fat .	51·95	47·29	40·70	38·50	..	..
Outside rump fat .	54·48	43·22	42·60	35·25	196·6	183·1
Outside rib fat . .	54·25	40·95	44·60	33·20	200·2	180·6
Same, inner layer .	49·35	45·95	38·70	35·35	202·3	199·2
Outside chuck fat .	46·68	..	38·95	..	199·1	..
Brisket fat . . .	59·75	49·82	35·50	33·85	206·1	..
Marrow fat . .	58·93	53·92	38·10	25·70	..	..

On the assumption that the fatty acids of tallow consist of palmitic, stearic, and oleic acids only, an assumption which may be considered as correct for all practical purposes, the composition of a sample may be arrived at by determining the proportion of stearic acid in a direct manner by the method described Vol. I. Chap. VIII. In the examination of several samples of tallow the author found from 21 to 22 per cent of stearic acid. The specimen examined by *Kreis and Hafner* (see table, p. 732), of the iodine value 35·8, gave 39·5 per cent of stearic acid.[1] *Link*[2] in a tallow of the iodine value 33 found solid acids 51·6 per cent containing 45 per cent of stearic acid, the melting point of which was 67·5° C. The total fatty acids contained 23·2 per cent of stearic acid. The proportion of oleic acid can be calculated from the iodine value ; the difference gives then the amount of palmitic acid. The variations in the percentage of stearic acid in beef fat from different parts of the body of the same animal are implicitly expressed by the percentages of " stearic acid " of solidifying point 54·8° C. given in the table, p. 637 of fourth edition. (It should, of course, be noted that the " stearic acid " includes palmitic acid.)

[1] It should, however, be noted that *Kreis and Hafner* did not determine the melting point of their "stearic acid," hence the figure 39·5 per cent must be accepted with reserve.

[2] Determined in the author's laboratory.

Physical and Chemical Characteristics of Beef Tallow

Specific Gravity		Solidifying Point		Melting Point		Saponification Value		Iodine Value		Reichert Value c.c. n/10 norm. KOH.	Thermal Test. Heat of Bromination.		Refractive Index.	
At °C.	Observer	°C.	Observer	°C.	Observer	Mgrms. KOH.	Observer	Per cent.	Observer		°C.	Observer	At 60° C.	Observer
15	0·943-0·952 Dieterich	35·27 Temperature rises a few degrees without, however, remaining constant.	Rudorff	45-46; 42; 43, not below 40	Wolkenhaar	195·7-200	Flisinger	40	Hübl	0·25	6·13	Archbutt	1·4510	Thorner
50	0·8950 Allen			47·6-48·5	Dieterich	193·2-198	Kottstorfer / Deering / L. Mayer	43·8-44	Wilson		6·7-7·2·4	,,	Butyro-refractometer "Degrees."	
98 (water 15·5=1)	0·8626 ,,			43·5-45	Rudorff			35·4-36·4	Flisinger				At 40° C.	Observer
100 (water 15·5=1)	·860-0·861 Wolkenhaar							35·6-38·9	Dieterich				49	Mansfeld
100 (water 15=1)	0·860 Koenigs							45·2-1	Wallenstein and Finck					
								38·82	Thorner					
								38-40	,,					
								41-47·5	Lewkowitsch					

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
Per cent.	Observer	At 100° C. (water at 100=1)	Observer	°C.	Observer	°C.	Observer	Mgrms. KOH.	Observer		Observer	Per cent.	Observer	At 60° C.	Observer
95·6	Bensemann / L. Mayer	0·8698	Archbutt	43·5-45	Dalican	43·44 and 46·47	Bensemann	197·2	Lewkowitsch	270-285	A. Wright	41·3	Williams	1·4375	Thörner
95·4-96				44·5	De Schepper and Geitel	45	Hübl	201·6	Thörner			25·9-32·8	Morawski and Dennski	Oleo-refractometer "Degrees."	
				43	Hübl							Iodine Value of the Liquid Fatty Acids.			Observer
				Op. Chap. VIII.	Lewkowitsch							92·41	Wallenstein and Finck	-40	Jean
												92·22	,,		

1 Australian.   2 Berlin town tallow.   3 American beef.   4 Home-refined.

It has been pointed out already that tallow frequently undergoes a "demargarinating process," by being subjected to pressure in hydraulic presses, when "beef stearine" and "tallow oil" are obtained (see p. 764).

Beef stearine differs in its chemical composition, not only owing to the variation of different specimens of tallow, but also with the pressure applied in the hydraulic press and with the length of time during which the pressure has been allowed to act on the tallow. Commercial samples of beef stearine have melting points varying, as a rule, from 49° to 53° C. The iodine value varies from 8 to 15 and even to 20 and the percentage of stearic acid rises in inverse ratio to the decrease of the iodine value ; thus *Hehner and Mitchell* found in a beef stearine absorbing 2·0 per cent of iodine 50·2-51·1 per cent of stearic acid. Recently *Bomer* [1] has shown that by frequently repeated crystallisation of beef stearine from ether approximately 4·5 per cent of pure tristearin can be isolated. It should be noted that beef stearine is more soluble in petroleum ether (of specific gravity 0·648) and methylated ether (of specific gravity 0·7175) than is lard stearine (*Dunlop*). This is of importance in the detection of beef stearine in lard (cp. "Lard," tables, p. 732).

Beef stearine obtained from "premier jus" is used for edible purposes in the manufacture of margarine, as also in the manufacture of compound lards and in the preparation of "suet substitutes" (see Vol. III. Chap. XV.).

The amount of free fatty acids in tallow varies considerably with the state of purity. In freshly rendered tallows the proportion of free fatty acids is negligible and rarely exceeds 0·5 per cent ; in commercial samples the percentage of free fatty acids may rise to 25 per cent and even more. Hence the acetyl values shown by tallows of different states of purity will also vary. Thus *Lewkowitsch* found acetyl values varying from 2·7 to 8·6 in different brands of tallow. It need hardly be repeated (cp. Vol. I. Chap. VI.) that these acetyl values do not indicate the presence of hydroxylated acids. In this connection it may be pointed out that *Fahrion* [2] found in a specimen of tallow 0·13 per cent of "oxidised" acids.

The valuation of "*premier jus*" and oleomargarine is based in the first instance on the taste and on the absence of free fatty acids and freedom from rancidity. Samples of oleomargarine examined by the author contained from 0·29 to 0·6 per cent of free fatty acids. Notwithstanding this amount of free fatty acids, these oleomargarines were perfectly suitable for the manufacture of margarine and other preparations intended for edible purposes. On reducing oleomargarine by *Paal and Roth's* method, Vol. I. p. 45, a hard crystalline almost tasteless mass was obtained which softened at 47° C., and melted completely at 55° C. Its iodine value was 1·2. The determination of the iodine value and of the melting point is of secondary importance and need only be resorted to if special circumstances demand examination

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.,* 1907, xiv. 111.
[2] *Zeitschr. f. angew. Chem.,* 1898, 784.

in this direction. With regard to the detection of colouring matters in edible tallow cp. p. 795 and Vol. III.

Tallow may be bleached by means of fuller's earth, or in some cases potassium dichromate and hydrochloric acid. Simple steaming with or without a small amount of caustic soda will sometimes cause the dark coloured colloidal impurities to coagulate and so settle out.

The valuation of commercial tallow for the purposes of soap- and candlemaking is based, in the first instance, apart from the colour, on the *proportion of water and non-fatty matter* and on the solidifying point (" titer ") of its fatty acids.

The proportion of water is determined in the usual manner. The following commercial method was introduced by *A. Norman Tate* :— Heat 50 grms. of the sample in a porcelain crucible or a silver crucible to 130° C. and keep it thereat until bubbles cease to be given off and the melted fat is in a condition of calm fusion without giving off vapours. The fat is then allowed to cool, and is weighed. The loss is calculated as moisture (cp. Vol. I. Chap. IV., also p. 751). In the case of pure fats *Tate's* method yields correct results. In the case of tallows with which lime soaps have been fraudulently admixed, the determination of the moisture by this method leads to too low results, as lime soaps retain moisture with great tenacity. This happens especially in the case of bone fats (cp. p. 751), as is shown by the following analyses, due to *Shukoff and Schestakoff* :—

<p align="center">*Moisture in Bone Fats*</p>

Usual Method. Per cent.					Norman Tate's Method. Per cent.
2·80	.	.	.	.	. 1·90
6·11	.	.	.	.	. 4·30

A. Norman Tate & Co., in a private communication to the editor, however, maintain the accuracy of their method, and adduce in support of their contention comparative tests with fats containing known amounts of lime soap and water.

Impurities—not fat—are determined as described, Vol. I. Chap. IV. (cp. also bone fat, p. 751). The titer test must be determined with due observance of the details given in Vol. I. Chap. VIII.

The higher the titer the more valuable is the tallow for the purposes of the candlemaker and soapmaker. The following empirical table compiled by *Dalican* is still used in a number of candle-works for an approximate estimation of the yield of commercial stearic acid from tallows having the solidifying points recorded in the first column of the table :—

<p align="right">[TABLE</p>

Solidifying Point. Titer Test.	Commercial Stearic Acid.	Oleic Acid.
° C	Per cent	Per cent.
35	25·20	69·80
35·5	26·40	68·60
36	27·30	67·70
36·5	28·75	66·25
37	29·80	65·20
37·5	30·60	64·40
38	31·25	63·75
38·5	32·15	62·85
39	33·44	61·55
39·5	34·30	60·80
40	35·15	59·85
40·5	36·10	58·90
41	38·00	57·00
41·5	38·95	56·05
42	39·90	55·10
42·5	42·75	52·27
43	43·70	51·30
43·5	44·65	50·35
44	47·50	47·50
44·5	49·10	45·60
45	51·30	43·70
45·5 [1]	52·25	42·75
46	53·20	41·80
46·5	55·10	39·90
47	57·95	37·05
47·5	58·90	36·10
48	61·75	33·25
48·5	66·50	28·50
49	71·25	23·75
49·5	72·20	22·80
50	75·05	19·95
50·5	77·10	17·90
51	79·50	15·50
51·5	81·90	13·10
52	84·00	11·00
52·5	88·30	6·70
53	92·10	2·90

Tallows of a lower titer than 44° C. are unprofitable to the candle-maker, and are therefore chiefly employed for soap-making.

A large amount of **free fatty acids** depreciates the value of a tallow considerably, as the candle material obtained from such tallow in the lime saponification process turns out dark ; also soap made from such tallow has an inferior (" foxy ") colour.

In the valuation of tallow for *lubricating purposes* the titer test is of secondary importance, whereas the determination of the amount of free fatty acids affords the necessary guidance.

Adulterants in tallow are easily detected by means of the quanti-tative reactions.[2] If required the phytosteryl acetate test may be

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[1] *Link* in a tallow having a titer test 45·3 and containing 23·2 per cent of stearic acid found 51·6 per cent of solid acids of the iodine value 9·5 and 45·6 per cent of liquid acids of the iodine value 63·5.

[2] The different behaviour of cocoa nut oil and palm kernel oil soaps from that of tallow soap to solutions of common salt and caustic alkalis has been frequently

applied for the detection of vegetable oils and fats. It must, however, be added that at present tallow is but rarely adulterated with vegetable oils or fats. A not infrequently used adulterant is " whale stearine," which will be shown by the high iodine value of the liquid fatty acids and also by the isolation of octobromides. Even paraffin wax has been used as an adulterant, particularly in tallow used for launching ships where hardness of texture is a desideratum. Home tallow is sometimes adulterated with *distilled grease stearine* (Chap. XVI.). Adulteration with waste fats is on the increase; high percentage of free fatty acids and high proportions of unsaponifiable matter indicate the adulteration. A tallow thus adulterated has a peculiar smell, a high acid value, and a somewhat high amount of unsaponifiable matter. If the latter after boiling with acetic anhydride and adding concentrated sulphuric acid exhibits a green fluorescence,[1] the presence of isocholesterol and, inferentially, of distilled grease stearine would be indicated. The fatty acids obtained from tallow thus adulterated turn yellow after a few days, and exhibit the peculiar smell characteristic of wool fat and its derivatives.

A high acid value may also point to admixed stearic acid (" cotton stearine ") from cotton seed mucilage (Chap. XVI.); in that case, of course, the isocholesterol reaction will not be obtained, but the acid value and the amount of unsaponifiable matter will be found to be high.[2]

Goat's tallow, sold in commerce as mutton tallow, is considered by candlemakers as an adulterant. Although such tallow has a high melting point, it is not suitable for candles, owing to its fatty acids not crystallising readily, but solidifying to an amorphous mass, from which it is difficult to remove the imprisoned oleic acid. The candles prepared in the ordinary way from goat's tallow are of low quality, do not possess the metallic ring of first-class candles, and easily become discoloured through their persistently retaining oleic acid. Goat's tallow is best detected by the smell given off on warming the sample (*Chevreul's* " acide hircique ").

This class of tallow plays an unimportant part in the world's market.

Analyses of fats from different parts of the American buffalo (bison) are given by *Schmidt* [3] in the following table :—

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employed as a means of detecting cocoa nut and palm nut oils in tallow. Such methods have been detailed in the second edition of this work, pp. 596, 597, but were omitted in the third edition, since they have been superseded by more expeditious methods. They are referred to here because the same principle has again been proposed recently (Cohn, *Chem. Zeit.*, 1907, 854).

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 142.

[2] In Germany paraffin oil is used by the custom-house officers for "denaturing" tallow if caustic soda be objected to. According to the regulations of the United States Department of Agriculture tallow which is unfit for edible purposes must be denatured either with sufficient kerosine (burning oil), or with coal-tar creosote, to give it a distinct taste of these substances, or with the colouring matter "Sudan III."

[3] *Journ. Ind. Eng. Chem.*, 1912, No. 8.

Name of Fat.	Specific Gravity at 15°.	Saponifica- tion Value.	Iodine Value (Wijs).	Free Fatty Acids. Per cent.	Titer Test. °C.
Caul fat . . .	0·9263	200·6	33·23	0·90	50·1
Kidney fat . .	0·9346	199·3	29·45	1·65	52·2
Ruffle fat . .	0·9364	199·4	32·50	1·90	51·0
Paunch fat . .	0·9244	204·2	34·92	1·50	47·4
Chip fat . . .	0·9344	199·5	35·16	1·25	49·6

For the fat obtained from the Indian buffalo cp. " Butter fat," p. 807.

MUTTON TALLOW

French—*Suif de mouton.*   German—*Hammeltalg.*
Italian—*Sego di montone.*

For tables of characteristics see pp. 774, 775.

Mutton tallow closely resembles beef tallow ; it is frequently mixed with the latter and is then sold as " mixed tallow."   Mutton tallow is as a rule harder than beef tallow, and consequently its solidifying and melting points, as also those of its fatty acids, are higher ; it is more liable to turn rancid than is beef tallow, and has as a rule a " stronger," more unpleasant flavour than beef tallow.   For this reason it cannot be used in the manufacture of first-class butter-substitutes or high-class toilet soaps.

Recently *Bömer* [1] has shown that by frequently repeated crystal-lisation of mutton tallow from ether approximately 3 per cent of pure tristearin and of 4-5 per cent each of stearo-dipalmitin (dipalmito-stearin) and of palmito-distearin can be isolated (cp. Chap. XII.).

Mutton " stearine " behaves with solvents (petroleum ether and ordinary ether) much like beef stearine (cp. tables under " Lard ").

The fat rendered from different parts of two sheep gave, according to *Moser*,[2] the following results :—

Fat from	Fat.			Fatty Acids.	
	Solidifying Point	Melting Point	Saponification Value.	Solidifying Point	Melting Point.
	°C.	°C.		°C.	°C.
Kidneys . . .	40·7-40·9	51·0-55·0	194 8-195 2	51·9-51·9	56·2-56 5
Caul and intestines .	39·2-39·7	52 0-52·9	194·6-194·8	50·4-50·6	54·9-55 8
Adipose tissue .	34·1-34·9	49·5-49·6	194·2-194·4	43·7-46·2	50·7-51 1

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiv. 116 ; 1909, xvii. 396.
[2] *Bericht der Thätigkeit der Landw.-Versuchsst. Wien,* 1882, 1883.

Physical and Chemical Characteristics of Mutton Tallow

Specific Gravity		Solidifying Point.		Melting Point.		Saponification Value.	
At ° C.	Observer.	° C	Observer.	° C.	Observer.	Mgrms KOH.	Observer.
15	Dieterich	36-32 (rising several degrees)	Rudorf	47-49	Dieterich	192-195·2	Thorner
100 ,,	Koenigs		Thorner	46·5-47·4	Rudorf		
	Thorner	40-41		44-45	Thorner		
0·937-0·953							
0·860							
0·858							

Physical and Chemical Characteristics of Mutton Tallow—continued

Iodine Value		Thermal Test. Heat of Bromination.		Refractive Index.	
Per cent.	Observer.	° C	Observer.	At 40° C	Observer.
35·2-46·2	Wilson	8 1 [1]	Hehner and Mitchell	1·4501	Thorner
34·8-37·7	Dieterich	7 6 [2]	Archbutt		
32·7	Thorner	7 55 [3]	,,		
43-44	Wallenstein and Finck	8 9 [4]	,,		
38·6					

[1] From kidney.   [2] From flare.   [3] Australian mutton.   [4] Home-refined.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
Per cent.	Observer.	°C.	Observer	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
95·54	Bensemann	41 39	Thorner ,,	49-50 and 53-54 49 46-47	Bensemann Thorner ,,	198	Lewkowitsch	34·8	Thorner	1·4374	Thorner
		Titer Test									
		45-46 also 43·2 46·1 See Chap. VIII.	Dalican de Schepper and Geitel Lewkowitsch					92·7	Iodine Value of the Liquid Fatty Acids Wallenstein and Finck		

A specimen of mutton tallow of the iodine value 42·5 contained 35·5 per cent of stearic acid [1] (*Kreis and Hafner*).

The information contained in the following table, due to *Hehner and Mitchell*,[2] is very instructive ; the different specimens of fat were taken from a Scotch sheep eighteen months old :—

Fat from	Iodine Value.	Melting Point of Fatty Acids.	Stearic Acid.
	Per cent.	° C.	Per cent.
Kidneys . .	48·16	45·6	26·2-27·7
Back . .	61·3	41·4	24·8
Neck . .	48·6	42·2	16·4
Breast . .	58·2	33·8	About 1
Ham . .	50·6	40·8	No deposit after two days.

A special kind of mutton tallow is " graisse de couyrouck " obtained from the extraordinarily developed caudal appendix of a Turkish sheep.

BUTTER FAT

French—*Beurre de vache*.   German—*Butterfett*.
Italian—*Burro di vacca*.

Butter fat or milk fat is contained in cow's milk.

Egyptian butter prepared by the natives is also largely admixed with the milk fat from the buffalo, sheep, and goat.[3]

The production of butter on the farm is one of the oldest house industries, and is so well known that it requires no description here. Moreover, as a house industry it is rapidly dying out in the densely populated countries, not only on account of the naturally limited amount of milk that can be provided for this purpose in any one locality, but also because the essential conditions for butter production, viz. cleanliness and cooling arrangements, cannot be attained readily.   The house industry is rapidly giving way in all butter-producing countries to a large scale manufacture in *creameries, i.e.* establishments which collect the fresh milk from a number of farms and work it up into butter. These creameries may well be likened to a factory dealing with the production of edible oils and fats.   In these factories the chief essentials on which successful manufacture rests can be scrupulously observed. The milk is received in the freshest state possible, pasteurised if necessary, and the cream separated by *milk séparators*,[4] which are either worked

[1] It should, however, be noted that *Kreis and Hafner* did not determine the melting point of their "stearic acid," hence the figure 35·5 per cent must be accepted with reserve.

[2] *Analyst*, 1896, 327.

[3] *Cairo Scientific Journ.*, 1911, 297.

[4] For a Canadian "butter separator," cp. *Canada, Department of Agriculture, Central Experimental Farm, Ottawa, Ont., 1906*, Ottawa, 1907.

by hand or are belt-driven. The best-known belt-driven machines are the Alpha-Laval cream separators, which furnish in the form of cream the largest amount of the fat contained in the milk.[1] It is recommended to sterilise the milk intended for butter and cheese-making by heating to 60° C. for 20 minutes which is said to be sufficient to destroy the tubercle bacilli.[2] The ripening of the cream[3] (either by naturally prepared " starters " or by " pure culture starters ") is also carried out in these establishments with scrupulous cleanliness which is hardly practicable in a farm-house. The churning[4] of the ripened cream is practically a mechanical process and consists in causing the butter fat globules to coalesce and so to form the commercial butter ; it is carried out in these establishments on a manufacturing scale, as is also the washing[5] and the " working " of the butter on the " butter table." The object of these latter operations is to remove as far as possible the milk which is detrimental to the keeping of the butter. Frye[6] patents a process whereby the cream is subjected to an electric current which is stated to cause the fat globules to coalesce. On the butter table, if required, salt also is added. The machinery employed throughout is similar to that described under " Margarine Manufacture," Chap. XV. In fact, it may be said that the greatest impetus has been given to the production of butter on a manufacturing scale through, the margarine manufacture.

Butter produced in these establishments is known as "creamery butter."

In consequence, of the insufficiency of the European home production, enormous amounts of butter are imported into Europe. A large quantity of such butter is sold in its original form. By no means insignificant amounts are, however, " blended " in " butter factories " with home-produced butter on butter tables (see Fig. 1, Vol. III.), or in mixing machines. The mixture is still, of course, butter, but it can be differentiated from " creamery " butter by its different " grain " or " texture," the natural, smooth grain of the once finished butter having been " broken " by the mixing together, on the butter table, of the foreign butter with butter produced in creameries.

Such butter is known as " factory butter."[7] The keeping qualities of factory butter are inferior to creamery butter.

With the increased production of butter the difference between

[1] For the recovery of fat from the butter milk cp. Luning, Swedish patent 35,535.

[2] *United States Dept. Agric. Bureau of Animal Industry*, 1909, 179.

[3] Special ripening machines of tinned copper are made by E. Ahlborn, Hildesheim. Contact with iron is said to give the butter an unpleasant metallic flavour.

[4] E. and H. H. Schou (English patent 5810, 1908) dispense with churning by passing ripened cream over chilled rollers. Cp. also A. H. Borgstrom ; English patent 6394, 1907, French patent 387,653 (1908).

[5] Washing with water of an impure character may cause rancidity ; hence it is recommended to sterilise the water by means of the uviol light (Dornie and Dairie). *Chem. Zentralbl.*, 1909 (ii.), 1001. The ultra-violet rays have also been used for sterilising the butter itself ; cp. French patent 400,921 (*Société le Ferment*).

[6] French patent 389,836.

[7] According to another definition, "factory butter" is made by the old process of putting milk in dishes and allowing the cream to rise before separating, whereas "creamery butter" is obtained from milk by the aid of centrifugal apparatus.

"creamery butter" and "factory butter" tends to disappear more and more. Some of the largest creameries can now hardly be differentiated from factories, the creamery butter produced by them being only a small fraction of their total output of butter. Even creameries have, therefore, commenced to add to their butter boric acid as a preservative, so that one characteristic difference that once distinguished creamery butter from factory butter has practically ceased to exist. Indeed, creameries no longer guarantee the whole of their output as free from boric acid, a warranty in that respect being only given for limited amounts sold at a higher price.

Even in oversea countries the necessity has arisen for collecting the produce of a number of farms and blending it in central establishments. In New Zealand these establishments are termed "packing-houses," and the butter prepared there is shipped as "milled butter," this word having been chosen to distinguish this butter from creamery and factory butters.

The chief butter exporting countries of Europe are Denmark, Russia, Holland, France, and Sweden.

Home Production, Exports and Imports, of Butter of several European Countries

Country.	Home Production (Estimated)	Exports				Imports			
		1902	1904	1910	1911	1902	1904	1910	1911.
	Tons.	Tons.	Tons.	Tons	Tons	Tons	Tons.	Tons	Tons.
Denmark	..	69,770	81,530	..	..	7000	5900	..	143
Russia .	..	37,821	39,492	1,503	2,079	245	360	..	..
Holland .	60,000[1]	22,861[2]	23,607	33,283	31,013	680	2654	2493	2739
France[3] .	130,000	24,041	22,628	24,936	13,204	5462	4567	5107	9541
Sweden .	..	20,054	19,570	..	..	521	592	..	..

Smaller quantities of butter are exported from Norway, Italy, and Belgium. The exports from Siberia were in 1912 75,000 and in 1913 86,000 tons. Germany has practically ceased to be a butter-exporting country, and she now imports considerable quantities from Denmark, Holland, Sweden, Finland, Siberia, and oversea countries.

The imports into and exports from Germany are as follows :—

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[1] In 1908 64,000, of which 41,000 is "Dutch control."
[2] In 1908 to Germany 14,900 tons.
[3] Fuller details will be found in Lewkowitsch, *Technologie et analyse chimiques des huiles, graisses et cires,* traduit par E. Boutoux, p. 1262.

❋	Imports.	Exports.
	Tons	Tons.
1902	16,689	2199
1904	34,399	801
1908	33,849	218
1909	44,058	204
1910	41,427	181
1911	55,398	252

The importance which Finland has gained as a butter-exporting country may be gathered from the following table :—

Exports of Butter from Hango, Finland

	1904.	1905.	1906.	1911.	1912.
	Cwts	Cwts.	Cwts	Kilogrammes	Kilogrammes.
To Great Britain .	183,392	224,540	232,516	8,534,497	7,513,839
„ Denmark . .	42,795	56,705	38,845	660,257	227,661
„ Other countries .	5,992	22,800	15,547	3,156,565	4,269,869
	232,179	304,045	286,908	12,351,319	12,008,369

The amount of butter produced in the United Kingdom in the three years 1903 to 1905 averaged 163,140 tons, while the average annual imports less exports were 203,301 tons. The average quantity consumed per head of population, calculated from these figures, was as follows :—

Home-produced butter	.	.	.	8·5 lbs.
Imported butter	.	.	.	10·7 lbs.
Total	.	.	.	19·2 lbs.

Large quantities of butter are now imported into Europe from Australia, Canada, the Argentine, New Zealand, and Siberia.

The importance which the butter trade has acquired in the world's market may be best illustrated by the following table which deals with the United Kingdom, the chief butter-importing country of Europe :—

[TABLE

Imports of Butter to the United Kingdom

	1903.	1904.	1905.	1906.	1907.	1908.	1909.	1910.	1911.	1912.
Quantities in cwts.	4,027,766	4,254,185	4,157,778	4,344,346	4,210,156	4,210,821	4,062,812	4,325,539	4,302,692	4,005,159
Value in £	20,798,707	21,117,162	21,586,662	23,400,196	22,417,926	24,080,912	22,424,962	24,493,450	24,600,619	24,354,193

Exports of Butter from the United Kingdom

	1903.	1904.	1905.	1906.	1907.	1908.	1909.	1910.	1911.	1912.
Quantities in cwts.	,191	9,566	9,062	12,966	12,305	10,045	9,216	9,244	11,928	11,342
Value in £	63,341	51,354	49,155	78,457	68,591	59,324	54,807	56,256	70,631	72,029

Re-exports of Butter from the United Kingdom

	1903.	1904.	1905.	1906.	1907.	1908.	1909.	1910.	1911.	1912.
Quantities in cwts.	63,511	86,666	70,518	77,504	83,591	55,078	72,315	68,344	135,552	119,021
Value in £	312,703	409,319	357,658	396,995	418,643	305,729	383,692	384,088	759,214	715,096

In order to show which countries are chiefly supplying the United Kingdom with butter I append the following table :—

Imports of Butter into the United Kingdom

Countries from which imported.[1]	Quantity. Cwts. 1906.	Quantity. Cwts. 1907.	Quantity. Cwts. 1908.	Quantity. Cwts. 1909.	Quantity. Cwts. 1910.	Quantity. Cwts. 1911.	Quantity. Cwts. 1912.
Foreign Countries :—							
Argentina	48,737	51,122	61,181	73,553	65,944	24,209	67,244
Belgium	42,239	22,120	...	...	...	...	...
Denmark	1,675,761	1,818,811	1,800,169	1,764,027	1,726,091	1,707,178	1,618,048
France	319,401	281,306	394,365	413,306	361,249	171,080	246,652
Germany	10,701	7,297	2,698	2,944	3,481	2,291	2,355
Iceland and Greenland	2,319	2,804	2,362	2,751	3,308	3,413	3,973
Italy	...	...	22,605	14,018	9,028	2,485	1,534
Netherlands	195,366	168,496	244,346	148,567	154,537	104,655	113,716
Norway	29,302	23,465	27,409	29,467	22,081	29,813	30,634
Russia	606,549	657,649	651,036	601,712	584,040	638,284	683,650
Sweden	182,803	226,740	284,364	312,142	345,684	360,357	335,014
Tripoli	23	...	...	...	...	...	...
Turkey	5	...	...	...	...	...	...
United States of America	157,312	1,063	44,333	693	756	23,052	2,596
Uruguay	160	...	1,087	348	94	239	119
Other foreign countries	...	...	...	...	...	...	...
Foreign Countries—Total	3,270,678	3,261,115	3,535,955	3,363,537	3,276,293	3,067,056	3,105,535
British Possessions :—							
New South Wales	180,655	195,289	...	...	...	...	...
Victoria	287,190	288,670	...	...	...	...	...
Queensland	77,982	97,685	...	...	...	...	...
South Australia	15,287	17,342	...	...	...	...	...
Australia—Total	561,114	598,986	409,106	396,986	667,966	896,085	543,396
Canada	190,968	34,753	43,084	22,522	16,805	61,936	27
Cape of Good Hope	977	...	...	...	...	...	...
Channel Islands	1	...	...	...	...	...	...
Indies, East, British	1,848	1,439	1,268	774	1,767	1,163	924
New Zealand	311,672	313,863	221,395	278,581	362,674	276,446	349,012
Other British Possessions	...	...	13	412	34	6	265
British Possessions—Total	1,066,580	949,041	674,866	699,275	1,049,246	1,235,636	899,624
Total	4,337,258	4,210,156	4,210,821	4,062,812	4,325,539	4,302,692	4,005,159

[1] The countries named above are those from which the quantities shown were received and are not necessarily the countries of origin.

The total amount of butter produced in Australia during the years 1902-11 was as follows :—

Year.						Lbs.
1902	.	.	.	.	.	.	79,572,327
1903	.	.	.	.	.	.	100,332,242
1904	.	.	.	.	.	.	140,255,208
1905	.	.,	.	.	.	.	140,898,726
1906	.	.	.	.	.	.	159,870,662
1907	.	.	.	.	.	.	156,380,670
1908	.	.	.	.	.	.	145,317,357
1909	.	.	.	,.	.	.	154,273,252
1910	.	.	.	.	.	.	193,211,909
1911	.	.	.	.	.	.	211,577,745

The exports of butter from Canada are gradually decreasing.

Further statistical data regarding New Zealand and Siberia will be found below.

The examination of butter divides itself naturally into two parts : (I.) The examination of the whole butter; (II.) The examination of the butter fat.

Under the first heading I shall consider the examination of butter on the assumption that the fat contained in it is genuine milk fat.

I. Examination of Butter

Butter must be looked upon as an emulsion of fat and water containing small quantities of " casein " (" curd "), milk sugar, and inorganic salts. In those butters which are salted in the last stage of the manufacturing operation common salt will also be found. The following table, due to *Vieth*, gives a number of analyses of butter :—

Origin of Butter.	Fat.	Curd.	Salt.	Water.
	Per cent.	Per cent.	Per cent.	Per cent.
English . .	86·85	0·59	1·02	11·54
French . .	84·77	1·38	0·09	13·76
,, salted .	84·34	1·60	2·01	12·05
German . .	85·24	1·17	1·35	12·24
Danish . .	83·41	1·30	1·87	13·42
Swedish . .	83·89	1·33	2·03	13·75

The percentages of fat given in the last table vary within somewhat narrow limits, as the percentages of water do not differ widely. Butters containing as much as 90 per cent of fat are rarely met with. The percentage of fat in commercial butters rather tends to fall to the neighbourhood of 80 per cent, inasmuch as the maximum percentage of water which butter may contain has been legally fixed in many countries at 16 per cent. Naturally, the tendency is, especially in

butter factories, to regulate the composition of the product so that it may contain as high a percentage of water as the particular circumstances—nature of raw material, time of the year, etc.—permit.

With regard to butter having exceptional percentages of water see p. 784.

The examination of butter comprises the determination of **water, solids-not-fat,** and the detection of **colouring matters** and **preservatives.** Gross adulterants, such as *starch, potato pulp, ground white cheese,* etc., will hardly occur at present, since the sophistication of butter has assumed a more scientific character, and is practically confined to the addition of foreign fats. The adulteration with foreign fats will be considered under " 11. Examination of Butter fat " (p. 801).

1. **Water** is determined by drying a properly drawn average sample (cp. Chap. 1V.) at 100° C. The Society of Bavarian Analytical Chemists recommend drying the butter at 100° C. for six hours, with occasional stirring. This would appear far too long a time for so simple a determination. Moreover, this *modus operandi* is liable to lead to errors, as, on the one hand, loss may occur through volatilisation of any free fatty acids, and on the other hand, an increase of weight may take place through their oxidation. The method of *Henzold,* described Vol. 1. Chap. 1V., has, therefore, come more into vogue, especially in Germany, but even in this method the heating for two hours appears to be somewhat long. No doubt every analyst will be able to settle so simple a question by his own experience.[1]

Rivett [2] describes a process of the determination of water by treating a fat with calcium carbide and weighing the liberated acetylene by difference. He gives the figure 0·696 grms. of acetylene for each grm. of water. This process is said to yield concordant results, lower by about 0·3 per cent than the ordinary heating method.

In cases where scientific accuracy is not the chief object, as for market control, the amount of water may be determined rapidly by *Birnbaum's* method as modified by *Wibel* [3] in the following manner : 10 grms. of butter are shaken up with 30 c.c. of ether, previously saturated with water, in a tube corked at one end and provided with a stop-cock at the other, through which the separated aqueous liquid is run off into a second narrow graduated tube, containing 5 c.c. of saturated brine and a trace of acetic acid, so as to give a distinct red colour with litmus. The increase of volume, due to the water in the butter, is then read off. The results are stated to be but slightly below those obtained by gravimetric analysis.[4]

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[1] For *Crismer's* method of determining the amount of water by means of the critical temperature of dissolution the reader must be referred to the *Bull. de l'Assoc. Belge des Chim.,* 1896 (9), 359 ; *Analyst,* 1896, 241. Cp. A. Schoonjan's *Bull. Soc. Chim. Belg.,* 1908, 342. *Jean Bartholomé* says : It iodine value is low and saponification value high, the fatty matter is likely to return the largest amount of water.

[2] *Chem. News,* 1911, 261 ; cp. also Jungkunz, *Chem. Zeit.,* 1914, 91.

[3] *Journ. Soc. Chem. Ind.,* 1893, 630.

[4] Cp. also Poda, *Zeits. f. Unters. d. Nahrgs- u. Genussm.,* 1901, 492 ; F. Bengen, *ibid.,* 1908 (xv.), 587. G. R. Geldard, English patent 18,496, 1902 ; M. Vogtherr, French patent 324,745, 1902. With regard to Nicholls' "Sensible Apparatus" see A. Wingler and J. v. Sury, *Chem. Zeit.,* 1908, 1140.

Many other rapid methods and apparatus have been proposed. Their description necessarily falls outside the scope of this work, as they are unable—and indeed do not pretend—to furnish accurate quantitative results.

The proportion of water in butter depends to a large extent on the skill of the producer, shown by observing the proper temperature and regulating the final stages of the " working " of the butter so as to eliminate as much water as possible. As the knowledge of proper modes of manufacturing is being spread through dairy schools, and suitable appliances for expressing the excess of water are being introduced largely, the proportion of water in European butters lies now mostly between 11 and 14 per cent, although it may rise to 16 per cent. From figures derived from 111 samples of butter made in Northern France 97 contained 16 per cent and under of water, 10 from 16 to 18 per cent, 2 from 18 to 19 per cent, the remaining 2 contained 20·5 and 23·3 per cent of water respectively.

If butter is made at a somewhat high temperature—as is the case in the West of Ireland—the water cannot be removed so readily as in dairies in which the cream is cooled properly; the proportion of water in " Irish butter " is therefore high, rising to 25 per cent and more.

In this country the limit of 16 per cent for the proportion of water in butter has been legalised, and such exceptional butter as Irish butter may only be sold provided a sufficient disclosure is made to the purchaser.

Some butters imported from abroad have a low percentage of water (see below) and are, therefore, dry and hard owing to their having been kept in cold storage, and difficult to handle in the retail trade. In consequence of this difficulty there has sprung up a trade, the object of which is to incorporate water with such butters. Under the pretence of making such butters—chiefly colonial butters—more easy to handle in the retail trade, there is sold under the name of **milk-blended butter** an artificially prepared butter, containing from 20 to 25 per cent of water. It is manufactured by mixing skimmed milk or whole cream with butter, and adding preservatives so as to prevent the milk from " souring." It is evident that this is tantamount to incorporating water with butter. At first this adulterated butter was sold as " butter," but owing to the interference of the law the name was changed into " milk-blended butter." [1]

According to the " Butter and Margarine Act " of 1907 the sale of milk-blended butter is permitted in this country provided this butter contains no more than 24 per cent of water. I append a few analyses of " milk-blended " butters :—

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[1] Although this mixture of milk and butter had been the subject of numerous prosecutions under the Sale of Food and Drugs Acts, no High Court decision had been given in this matter, so that it was held that the seller of milk-blended butter was protected provided that a sufficient disclosure had been made to the purchaser at the time of sale.

Analysis of Milk-Blended Butters [1]

				Per cent.	Per cent.	Per cent.
Water	.	.	.	25·1	22·6	21·1
Fat	.	.	.	65·2	73·0	73·1
Casein	.	.	.	7·0	2·8	2·7
Salt, etc.	.	.	.	2·7	1·6	3·1
				100	100	100
Reichert-Meissl value of fat	.	.			34·4	31·3

In the following tables I give a number of analyses stating the percentages of water in commercial butters. The numbers of the following table (*Vieth* and *H. D. Richmond*[2]) are arranged by the author according to the percentages of water :—

Kind of Butter.	Number of Samples examined.	Samples containing per cent of Water.			Observer.
		From 11-14	From 10-15	Above 16.	
		Per cent.	Per cent.	Per cent	
English and foreign	560	83·8	94·2	0·9	Vieth
English	143	70·7	85·4	0·7	H. D Richmond
Foreign	417	88 3	97·2	1·0	,,
French	451	.		8·6	,,
,,	48			0·0	,,

In the following table *Martiny's*[3] numbers, referring to more than 20,000 separate analyses, are collated :—

Country.	Water. Per cent.	Number of Samples.
England .	11·18	334
Germany—		
Fresh butter .	13·96	523
Salt butter	13·01	1107
France	13·40	225
Denmark	13·99	9847
Sweden	13·66	4423
Finland	11·18	438

The percentages of water in imported butters (into England) are summarised in the following table (figures exceeding the permissible maximum of 16 per cent have been omitted from the first horizontal line) :—

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[1] F. Clowes, *Report from the Select Committee on Butter Trade*, 1906.
[2] *Analyst*, 1894, 17.   [3] *Landw. Jahrb.*, 1898, 773.

Origin.						Percentage.
Argentine, French, Italian	.	.	.		.	12-16
Danish	.	.	.	.	.	14-16
Canadian	.	.	.	.	.	12-16
Australian	.	.	.	.	.	12-15
New Zealand	.	.	.	.	.	9-15
Siberian	.	.	.	.	.	9-14

For purposes of " butter-blending " New Zealand and Siberian butters have assumed considerable importance. No doubt the fact that the law permits up to 16 per cent of water may induce the " butter-blenders " to add in " blending " so much water as to come as near as possible to the allowed limit. Undoubtedly some admixture of water is made,[1] and will be continued as long as the cost caused by the proper controlling of the percentage of water in the final product does not militate against this practice, but the extent to which this practice takes place seems to be magnified to an enormous degree in the imagination of those who are not acquainted with the conditions underlying manufacturing processes. Since butter-blending is considered in the eyes of the law a legitimate industry, it is impossible to trace the addition (if any) of water made in the " blending process."

In order to show what quantities of butters low in contents of water are available, I give the following statistical data referring to New Zealand butter :—

Export of Butter from New Zealand

Year.	Tons.	Value.
1886	1,159	£105,537
1887	850	54,921
1888	1,499	118,252
1889	1,898	146,840
1890	1,741	122,701
1891	1,972	150,258
1892	2,697	227,162
1893	2,907	254,645
1894	3,039	251,280
1895	2,898	227,601
1896	3,567	281,716
1897	4,950	402,605
1898	4,840	403,690
1899	6,804	571,799
1900	8,629	740,620
1901	10,080	882,406
1902	12,699	1,205,802
1903	14,255	1,318,067
1904	15,718	1,380,460
1905	17,143	1,514,156
1907	...	1,615,622
1908	11,493	1,171,182
1909	16,055	1,639,380
1910	17,826	1,811,975
1911	15,119	1,576,917

[1] Cp. *Revue intern. des falsific.*, 1907 (20), 97.

The first creameries in *Siberia* were opened in 1893, and since then their number has increased to a great extent. The export of butter from Siberia to Europe has increased from 5,416,800 lbs. in 1899 to 90,280,000 lbs. in 1902. (Even this did not represent the total export from Siberia, as considerable quantities had been sent to China and Japan. The exports in 1912 were 168,236,000 lbs., and in 1913 192,840,720 lbs. With the improved conditions of transport and the introduction of proper methods of dairying, even in the villages of the Altai mountains, the Siberian export has risen rapidly.)

2. **Solids - not - fat** are best determined in the sample of butter previously employed for the estimation of water, by exhausting the dried butter with ether, chloroform, carbon bisulphide, or petroleum ether, and weighing the residue after drying.

If a fresh quantity of butter be taken for this determination, due attention must be paid to the fact that butter is not a homogeneous product, as different parts of the sample contain varying amounts of butter-milk.

The solids-not-fat consist of *casein, milk-sugar,* aud *inorganic salts.* By exhausting the dried residue with water, to which a trace of acetic acid has been added, milk-sugar and the bulk of the inorganic salts are removed, leaving casein behind; its weight is ascertained after drying. The minute quantity of salts retained in the casein and found on incineration is then deducted. *Koenig* suggested to determine the proportion of nitrogen by *Kjeldahl's* process and multiply the result by 6·25. Both methods yield identical results. The aldehyde titration method of *Richmond and Miller* [1] has been applied by *Miller* to the analysis of butter. The method is as follows :—10 grms. of butter are weighed into a tared beaker and melted at about 60° C. ; 25 c.c. of water at 65° C. are added and the mixture agitated and rendered faintly alkaline to phenolphthalein with $\frac{n}{20}$ alkali; 5 c.c. of concentrated formaldehyde solution are added and the mixture well agitated and neutralised with $\frac{n}{20}$ strontium hydroxide solution. The difference between the number of c.c. used in the second titration and that required by the formaldehyde is proportional to the quantity of protein present, each c.c. representing 0·01355 grm. of protein nitrogen, assuming that the relation of casein to albumen is as 7 : 1. The extreme errors of the method are given as +0·02 and −0·025, compared with the Kjeldahl method when using as a factor 6·38. The proportion of casein (curd) in butter varies according to the length of time the milk (or the cream) has been allowed to stand previous to churning. The percentages found vary, as a rule, between 0·5 and 2·25 per cent. The figure 4·78 recorded by *Koenig* must be considered an exceptional one. *Sammis* [2] of the Wisconsin Agric. Expt. Station describes a method for the preparation of curd from butter-milk. For details the reader must be referred to the original communication.

The amount of casein (curd) has latterly become of some import-

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[1] *Analyst,* 1912, 50.

[2] *Journ. Ind. Eng. Chem.,* 1910, 142.

ance, as adulteration of butter has been carried out by means of curd obtained from milk (either by coagulating it with the help of rennet or by adding a little dilute hydrochloric acid, pressing the separated curd and converting it, with the assistance of sodium carbonate, into a jelly). The addition of such curd permits the butter to retain an increased amount of water without its becoming readily noticeable unless recourse be had to chemical analysis. Any butter containing more than 2 per cent of curd should be looked upon with suspicion.

The following is the analysis of an adulterant of this kind[1] :—

						Per cent.
Water	.	.	.	.	.	65·46
Fat	.	.	.	.	.	0·08
Sugar	.	.	.	.	.	2·24
Soluble proteids	.	.	.	.	.	0·69
Ash of soluble portion	.	.	.	.		0·35
Ash of insoluble portion		.	.	.		0·67
Casein by difference	.	.	.	.		30·5

A genuine butter containing 0·23 per cent of casein and 11·51 per cent of water showed, after admixture of 5 per cent commercial casein, 0·90 per cent of curd and 16·02 per cent of water.

The amount of *inorganic salts*, chiefly sodium chloride, is found by igniting the ether-insoluble residue from 10 grms. of butter, taking care, however, not to heat the ash to too high a temperature lest sodium chloride should volatilise. The proportion of sodium chloride is ascertained by titration with standard silver solution, using potassium chromate as an indicator. Sodium chloride is determined with greater accuracy by melting in a porcelain dish 10 grms. of butter with an equal amount of paraffin wax and 50 c.c. of water, previously acidulated with a few drops of nitric acid, and stirring the melted mass. After cooling, the cake is taken off and rinsed carefully, the aqueous liquid is then filtered, silver nitrate added, and the precipitated silver chloride weighed in the usual manner.

The proportion of sodium chloride in 113 samples examined by *J. Bell* was found lying between 0·4 and 9·20, the majority of the samples yielding from 2 to 7 per cent; only in one case 15·08 per cent was found. The amount of salt added to butter varies, of course, in different countries and localities. An excessive amount of ash will naturally invite further examination.

Milk-sugar is not determined direct, but found by difference.

Fraudulently added substances of a non-fatty nature, such as *starch, borax*, etc., are detected as described Vol. I. Chap. IV.

The proportion of **butter fat** is likewise found by difference; it can, of course, be determined direct by evaporating the ether-extract and weighing the residue.[2]

[1] *Analyst*, 1906, 177.
[2] With regard to Gottlieb's method, cp. *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905, x. 287; Hesse, *Chem. Zentralbl.*, 1905, i. 124. Cp. also Shaw, United States patent 1,052,098.

A rapid method for the direct determination of butter fat in butter is given by *König* [1] as follows :—1 grm. of the butter is placed in a stoppered cylinder of 200 c.c. capacity and 9 c.c. of hot water are added. When the butter is melted, 2 c.c. of ammonia, 10 o.c. of alcohol, 20 c.c. of ether, and 20 c.c. of petroleum ether are added. The cylinder is then shaken and the aqueous solution drawn off. About 0·4 grms. of powdered gum tragacanth is added, and after shaking, the ethereal solution is decanted into a weighed flask. The gelatinous mass is washed with petroleum ether, which is also added to the flask. The solvent is then evaporated and the residual butter fat dried and weighed.

3. **Preservatives.**—Well-made butter from which the butter-milk has been expressed carefully, and which has been washed properly, will remain " sweet " for a sufficient length of time. In the manu-facture of " *milk-blended* " butter the admixture of preservatives is a necessity, as the presence of milk—like that of all organic putrescible substances—tends to increase the liability of butter to become rancid, and at last unfit for consumption. In the case of carefully prepared home-produced butter the addition of preservatives, except perhaps pure salt (either as dry salt or as brine), is unnecessary.

A harmless preservative of butter is *salt*, and butter so preserved will keep for several weeks, and in cold storage even for months. Such butter is known in the trade as salt butter, to differentiate it from fresh butter, which is practically free from added salt. The latter butter is either sold in the fresh state, or preserved, by being kept (shipped) in cold storage.

With regard to the keeping properties of butter in cold storage cp. *W. S. Sayer, O. Rahn,* and *Bell Ferrand.* [2] With regard to the influence of salt on the micro-oganisms (bacteria, fungi) occurring in butter, and on the *optimum* percentage of salt, cp. *Q. Fettick.* [3]

Saltpetre is perhaps not so harmless as common salt. This pre-servative has not yet been the subject of extensive physiological ex-periments, although it seems to be used frequently in butters imported from oversea countries. [4]

Other preservatives are, however, frequently used to prevent rapid deterioration of butter which is made in a careless or uncleanly manner. Notwithstanding the fact that butter made in home dairies should not require the addition of any preservative, yet at certain seasons 0·25 per cent of boric acid is added even in well-conducted creameries. Colonial butter is usually preserved by the addition of a mixture of borax and boric acid, amounting in terms of boric acid to about 0·5 per cent, a quantity which has been approved of, as it were, by the Preservatives Committee (in England). In Italy the addition of 0·2 per cent of borax is permitted. In the Argentine the admixture of boric preservatives is forbidden.

With the importation of butter from foreign countries the necessity

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[1] *Apoth. Zeit.*, 1914, 223.   Cp. also Kropat, *Archiv d. Pharm.*, 1914 (252), 76.
[2] *Zentralbl. f. Bakterien u. Parasitenkund*, 1908, ii. 22.
[3] *Ibid.*, 1908, ii. 22, 32.
[4] Cp. Rohrig, *Molkerei Zeit.*, 1907, 1303.

of preserving it has become imperative, and salt has been replaced by other preservatives, some of which are considered inocuous, whereas others must be looked upon as dangerous to health and are, therefore, forbidden.

Amongst the first class of preservatives are included boric acid, borax, boroglycerin, glucose; amongst the second class formalin, benzoic acid and benzoates, and fluorides. Salicylic acid should be considered as standing midway between the two groups. Hence there arises the necessity for examining butter for the presence of these preservatives.[1]

Borax will be detected on examining the ether-insoluble portion.

Boric acid is detected by adding some caustic potash to 10 grms. of butter fat and incinerating in a platinum dish. The ash is acidified with hydrochloric acid, and tested with turmeric paper.

Richmond and Harrison [2] (using a slight modification of *Thomson's* method) recommended the following process :—About 25 grms. of butter are weighed in a stoppered cylinder ; enough water is added to make with the water already present 25 c.c., and then 10-15 c.c. of chloroform are added. The contents of the cylinder are warmed, mixed, and allowed to separate ; an aliquot portion of the aqueous solution is drawn off (each c.c. contains the boric acid in 1 grm. of butter), made alkaline, evaporated, ignited, and the ash extracted with hot water. The solution is made neutral to methylorange, boiled to expel carbon dioxide, and titrated with standard alkali after the addition of glycerol. That part of the ash which is insoluble is free from boric acid. For further details and improvements of this process (suggested by *Warren*) the original paper must be consulted.[3]

A more accurate gravimetric method for the determination of boric acid is given by *Partheil and Rose*.[4] This method has, moreover, the advantage that the boric acid can be obtained in substance.[5]

Opinions differ as to the harmlessness (or otherwise) of boric preservatives. Although this subject would appear to lie beyond the scope of this work, yet *Wiley's* [6] summary may be reproduced here. " It appears that both boric acid and borax when continuously administered in small doses for a long period, or when given in large quantities for a short period, create disturbance of appetite, digestion, and health." In order to show the extensive use made of boric acid the following notes taken from the Government Laboratory Report [7] may be added : Boron preservatives were found in 53·5 per cent of

[1] Stokes, *Analyst*, 1912, 178.
[2] *Analyst*, 1902, 179.
[3] *Ibid.*, 1902, 182.
[4] *Berichte*, 1901, 3611.
[5] For the German official method cp. Fendler, *Chem. Zeit.*, 1906, 108 ; *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1906 (xii.), 137 ; *ibid.*, 1908, xvi. 209. Cp. also Serger, *Chem. Zeit.*, 1911, 1127.
[6] *Influence of Food Preservatives and Artificial Colours on Digestion and Health. I.—Boric Acid and Borax*, by H. W. Wiley. Washington, U.S. Department of Agriculture, 1904. Cp. a criticism of Wiley's Report by Liebrich (Berlin, 1906, August Hirschwald), and L. Spiegel, *Chem. Zeit.*, 1907, 14.
[7] *Journ. Soc. Chem. Ind.*, 1907, 1081.

Canadian butters, 93·8 per cent of French butters, 93·6 per cent of Belgian butters, 83·3 per cent of Australian butters, 84·4 per cent of South American butters, 79·5 per cent of New Zealand butters; the percentages refer to the number of samples taken. Butters from southern countries in particular contained a preservative in excess of the amount recommended as the limit by the " Committee on the Preservatives in Food."

Glucose.—In the United States glucose is used as a preservative for export butter.[1] It is detected by washing the sample repeatedly with hot water and testing the aqueous layer with *Fehling's* solution. The fact should not, however, be overlooked that a *slight* reduction may be caused by milk-sugar or some of the albuminoids.

Salicylic acid is sometimes used to preserve butter.[2] It is detected by shaking the sample with twice its volume of 20 per cent alcohol and a few drops of dilute ferric chloride. In the presence of salicylic acid the aqueous layer shows a violet tint.[3]

Formalin (formaldehyde) is best detected by *Hehner's* method in the form given to it by *Richmond and Bosely* :[4] Add to the aqueous liquor, obtained when butter is melted, a drop of milk, and pour the mixture carefully on to the surface of concentrated sulphuric acid contained in a test-tube. In the presence of formalin a blue ring will appear at the zone of contact of the two liquids. A trace of ferric chloride renders the reaction far more distinct. The German official method directs to place 50 grms. of butter in a 250 c.c. flask together with 50 c.c. of water, to warm the mixture on the water-bath, and to distil off 25 c.c. in a current of steam. To 10 c.c. of the distillate 2 drops of an ammoniacal solution of silver nitrate are added, and the mixture allowed to stand in the dark. The presence of formalin is inferred from the reduction of the silver nitrate.[5] (The reaction described above is a general reaction of formaldehyde with proteins.) This method is, however, not free from objection, since butter made from ripened cream may contain volatile, silver-reducing substances.[6]

A new preservative sold commercially consists of a mixture of glucose and formic acid to which a small quantity of an ester is added, in order to mask the smell. Since at least 0·05 per cent of formic acid is necessary to act as a preservative, its detection is not difficult (*Richmond*[7]).

Saccharine has also been recommended for the preservation of butter. A method for its detection has been given by *Bianchi and Di Nola*[8] as follows :—The fat is saponified with alcoholic potash in the usual manner. The alcohol is driven off and the soap solution acidified with sulphuric acid. After removal of the fatty acids, the

[1] Crampton, *Journ. Amer. Chem. Soc.*, 1898, 201. *Analyst*, 1898, 130.
[2] *Journ. Soc Chem. Ind.*, 1887, 670 ; *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908 (xvi.), 209.
[3] Cp. also Barthe, *Bull. Soc. Chim.*, 1894, 516.
[4] *Analyst*, 1895, 155 ; 1896, 92, 94, 157.
[5] Cp. also T. Bokorny, *Chem. Zeit.*, 1909, 1141 and 1150.
[6] Cp. Mayrhofer, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1898 (xv.), 552.
[7] *Analyst*, 1898, 116 ; cp. *Zeits. f. Unters d. Nahrgs- u. Genussm.*, 1898 (xvi.), 226.
[8] *Boll. Chim. Farm.*, 1908, 47, 183.

aqueous solution is extracted with a mixture of ether and petroleum ether. The extract after distilling off the solvent is tested for saccharine.

Benzoic Acid and Benzoates.—These preservatives are now used on the Continent, especially for margarine.[1] *Wiley*[2] has drawn the conclusion from his extensive investigations of the subject that " in the interest of health benzoic acid and benzoate of soda should be excluded from food products." On the other hand an American Committee consisting of *Remsen, Long, Chittenden and Herter* have stated their opinion that sodium benzoate should be permitted as a preservative.

Gerlach[3] also states that benzoic acid has no toxic action on the human organism, hut its use as a preservative has heen condemned hy the Scientific Deputation of the German Agricultural Department. Since benzoic acid is volatile with aqueous vapours, a slight increase of the Reichert-Meissl value is caused thereby. This may he of special importance in the examination of margarine for the legally permissible limit of added hutter. Benzoic acid is detected in the first instance hy a somewhat high acid value of the butter fat. It will be best identified by isolating benzoic acid in substance,[4] and by the odour of its ethylester.

Fluorides have recently heen used as preservatives, especially for Brittany butter.[5] A "hutter preservative " is sold there which contains about 98 per cent of sodium fluoride.

The presence of fluorides is detected hy melting ahout 50 grms. of butter, separating the aqueous layer, rendering it alkaline, and evaporating the latter to dryness. The ignited residue is then treated in a platinum crucihle with strong sulphuric acid, the crucihle being covered with a wax-coated watch-glass, having a mark scratched in the wax. The crucihle is heated on a sand-bath for two hours. In the presence of even one mgrm. of calcium or sodium fluoride the glass will be found distinctly etched. A preservative examined hy *Bödtger*[6] consisted of potassium fluoride with a large quantity of silicic acid, which masked the usual test for fluoride. In order to detect fluorine the powder was heated with concentrated sulphuric acid and the vapours passed into water. The solution, after filtering off the

[1] Bemelmans, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiii. p. 492 ; Grimaldi, *Chem. Zeit.*, 1908, 794 ; Lehmann, *ibid.*, 1908, 949.

[2] *Influence of Food Preservatives and Artificial Colours on Digestion and Health. IV.—Benzoic Acid and Benzoates*, Washington, 1908. Cp. also K. B. Lehmann, *Chem. Zeit.*, 1908, 949, and 1911, 1297. Polenske, *Arb. a. d. Kaiserl. Gesundheitsamtes*, 1911, 149.

[3] *Physiologische Wirkung der Benzoesäure und des benzoesäurer Natriums.* Book written at the instance of the Association of German Margarine Manufacturers.

[4] A. E. Leach, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905, ix. 50 ; A. Röbrig, *ibid.*, 1908 ; W. v. Genersich, *ibid.*, 1908, xvi. 209 ; Halphen, *Journ. de Pharm. et de Chim.*, 1908, 201 ; L. Robin, *Annal. chim. analytique* (Genersich), 1908 (13), 431, and the critical review by Fischer and Gruenert, *Zeits. f. Unters. d. Nahrgs. u. Genussm.*, 1909 (xvii.), 721. The last-named authors advocate the conversion of benzoic acid into salicylic acid. Cp. also W. Friese, *Pharm. Zentralb.*, 1911, 1201.

[5] O. and C. W. Hehner, *Analyst*, 1902, 173.

[6] *Chem. Zeit.*, 1912, 105.

gelatinous silica, was precipitated with potassium carbonate, and the potassium silico fluoride tested in the usual manner.

Since in the presence of a boric preservative boron fluoride is evolved by strong sulphuric acid, the formation of boron fluoride must be prevented by the use of dilute sulphuric acid ; as long as the amount of boric acid does not exceed five times the amount of the fluoride present, the etching of the glass can be obtained. It is, however, preferable to remove the boron compounds at first. This is done by separating the aqueous liquor from 50 grms. of butter, adding calcium chloride, and heating to boiling after a small excess of sodium carbonate has been added. The precipitate (consisting of calcium borate, calcium fluoride, calcium carbonate, calcium phosphate, and perhaps traces of sulphate) is filtered off, ignited, and the residue treated with hot dilute acetic acid to remove the carbonate, borate, and phosphate. The residue is then filtered off, ignited, and treated with strong sulphuric acid as described above.

4. **Colouring Matter.**—Butter has no special colour of its own. That made during the time when the cows are on grass is yellow, whereas in winter when the cows are stall-fed the butter is almost white.[1] As the public demands a yellow butter, the product is as a rule coloured artificially before being placed on the market. The use of colouring matters, therefore, is not prohibited. (Butter which is naturally yellow is rapidly bleached when exposed to light and air.)

Foreign colouring matters, " butter colouring," are detected by shaking the melted butter with alcohol. In presence of foreign colouring matters the alcoholic layer becomes tinted, whereas natural butter leaves the alcohol colourless.

Moore[2] and *Martin*[3] recommend the use of a mixture of alcohol and carbon bisulphide. According to *Martin*, 5 grms. of butter are shaken with 25 c.c. of a mixture consisting of 15 parts of methyl alcohol, or ordinary alcohol, and 2 parts of carbon bisulphide. Two layers are formed ; the lower one consists of the fat dissolved in carbon bisulphide, the upper alcoholic layer contains the colouring matter.

Stebbins,[4] however, has pointed out that the small quantity of fat retained by the alcoholic layer may interfere with the subsequent examination, and that " carotin," the colouring matter from carrot juice, is more easily soluble in carbon bisulphide than in alcohol. He substitutes, therefore, the following process :—Melt 50 grms. of the sample in a beaker on the water-bath, stir into the melted mass 5 to 10 grms. of finely powdered fuller's earth, agitate thoroughly for two or three minutes, and allow to settle out completely whilst warm. Drain off the bulk of the fat, add 20 c.c. of benzene, stir well, allow to deposit, and decant the solution through a filter. Repeat this process until the fat is completely removed, and wash the precipitate on the filter

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[1] In this connection it may be interesting to note that in some Swiss farms having an abundant growth of *Leontodon* and *Ranunculus*, the cows gave butter of such intense yellow colour that suspicion was aroused ; the butter obtained after the second grazing was very much paler. In the United States also intensely yellow butter is met with.

[2] *Analyst*, 11, 163.   [3] *Ibid.*, 12, 70.

[4] *Journ. Amer. Chem. Soc.*, 1887, 41.

with benzene. Test the filtrates for carotin. Dry the precipitate on the water-bath, and boil out three times with about 20 c.c. of 94 per cent alcohol. Evaporate the alcoholic extracts in a tared dish, dry at 100° C., and weigh the residue. The residue obtained by either method is then examined by means of special reactions for the colouring matter suspected to be present.

Turmeric (*curcuma*) and annatto (notwithstanding the disgusting method by which the latter is prepared) are at present chiefly used in France. A preparation for colouring butter is sold there under the name of "jaune gras" ("fat yellow"), made by digesting annatto with sesamé oil and then adding turmeric.

Turmeric is indicated by the appearance of a brownish-yellow colouration on adding a few drops of ammonia, and of a reddish-brown colouration on subsequently adding hydrochloric acid.

Annatto is identified by a reddish-brown residue, which dissolves in concentrated sulphuric acid with production of a blue colour.

In the presence of *saffron* an orange-coloured precipitate is obtained on dropping lead acetate into the aqueous solution of the residue.

Harmless colouring matters are turmeric, annatto, carotin, marigold extract, and saffron. With regard to the last colouring matter it should, however, be noted that exhausted saffron, coloured yellow with an aniline dye, is frequently sold.

Aniline colours are, as a rule, poisonous, and should not be used for colouring butter.[1] According to *Frehse* auramine is occasionally used for colouring butter, and may be detected by the following test :— 1 c.c. of oil is saponified with 20 c.c. of an 8 per cent alcoholic soda solution with the addition of a little zinc dust. 50 c.c. of water are added and the solution shaken out with benzene. On dissolving the residue obtained from the benzene solution in glacial acetic acid, a blue colour is obtained.[2] A comprehensive scheme for testing for the various colouring matters has been worked out by *Leeds*.

Leeds [3] dissolves 100 grms. of butter in 300 c.c. of pure petroleum ether, of 0·638 specific gravity, in a separating funnel, draws off the curd and water, and washes several times with water, using about 100 c.c. The solution of butter fat is then kept at 0° C. for about twelve to fifteen hours, so that the bulk of the solid glycerides may crystallise out. The liquid fat is poured off and shaken with 50 c.c. of decinormal alkali, to remove the colouring matters from the ethereal solution. The aqueous layer is drawn off and carefully titrated with hydrochloric acid, until just acid to litmus. The colouring matters, containing a minute quantity of fatty acids, are thus precipitated ; the precipitate is transferred to a tared filter, washed with cold water, dried, and weighed.

For the discrimination of the several colouring matters the precipitate is dissolved in alcohol and two or three drops of the solution

[1] R. W. Cornelison, *Journ. Amer. Chem. Soc.*, 1908, 1478.
[2] *Ann. des. falsific.*, 1910 (3), 293. Cp. also Matthewson, *United States Dept. of Agric. Bureau of Chem.*, 1913, No. 113.
[3] *Analyst*, 1887, 150.

tested with an equal quantity of the reagents given in the following
table :—

Reactions of Colouring Matters

Colouring Matters	Concentrated H_2SO_4	Concentrated HNO_3	$H_2SO_4 + HNO_3$	Concentrated HCl.
Annatto	Indigo blue, changing to violet	Blue, becoming colourless on standing	Same	No change, or only slight dirty yellow and brown
Annatto + decolourised butter	Blue, becoming green, and slowly changing to violet	Blue, then green and bleached	Decolourised	No change, or only slight dirty yellow
Turmeric [1]	Pure violet	Violet	Violet	Violet, changing to original colour on evaporation of HCl
Turmeric + decolourised butter	Violet to purple	Violet to reddish violet	Same	Very fine violet
. Saffron	Violet to cobalt blue, changing to reddish brown	Light blue, changing to light reddish brown	Same	Yellow, changing to dirty yellow
Saffron + decolourised butter	Dark blue, changing quickly to reddish brown	Blue, through green to brown	Blue, quickly changing to purple	Yellow, becoming dirty yellow
Carrot	Umber brown	Decolourised	Do with NO_2 fumes and odour of burnt sugar	No change
Carrot + decolourised butter	Reddish brown to purple, similar to turmeric	Yellow, and decolourised	Same	Slightly brown
Marigold	Dark olive green, permanent	Blue, changing instantly to dirty yellow green	Green	Green to yellowish green
Safflower	Light brown	Partially decolourised	Decolourised	No change
Aniline yellow	Yellow	Yellow	Yellow	Yellow
Martins yellow	Pale yellow	Yellow, reddish precipitate. Magenta at margin	Yellow	Yellow, precipitate treated with NH_3 and ignited; deflagrates
Victoria yellow	Partially decolourised	Same	Same	Same, colour returns on neutralising with NH_3

[1] Ammonia gives with turmeric a reddish-brown colour which reverts to the original
colour on driving off the ammonia.

A scheme for the identification of colouring matters in foods by their behaviour with a solution of tannin and sodium acetate, hydrochloric acid, sodium hydroxide solution, basic lead acetate, and normal lead acetate has been devised by *Loomis*.[1] *Chapman and Siebold*[2] describe a method for the " adsorbtion " of colouring matters by mixing with kaolin. These authors state that colouring matters can be divided into three classes ; those which are completely " adsorbed," those which are partially " adsorbed," and which may be recovered from the kaolin by washing with water, and those which are not appreciably " adsorbed."

According to *Leffmann*,[3] methylorange is extensively used in the United States, especially for " oleomargarine." The colouring matter is extracted as described above and tested with dilute acid, when the well-known red tint will appear.

Geisler[4] states that annatto is now largely replaced in the United States by a yellow azo dye, which is used in combination with an orange dye (methylorange ?). The dye can be extracted from the fat by agitating with fuller's earth, from which the colouring matter in its turn can be extracted by boiling alcohol. The isolated dye dissolves in concentrated sulphuric acid giving a yellow colouration, which changes to red on the addition of water. (Methylorange does not behave in the same manner with fuller's earth.)

In the United States red palm oil also has been used as a colouring matter, the palm oil being incorporated with the help of cotton seed oil. (This colouring matter was chiefly used in the manufacture of " oleomargarine.") As the employment of this colouring matter is now prohibited by law, the methods which had been proposed for its detection need not be discussed here[5] (cp. also Vol. III. Chap. XV.).

Grünhut[6] proposes to detect colouring matters by dyeing wool with the extract. He saponifies the sample in the cold (Vol. I. Chap. II.), evaporates off the petroleum ether and the bulk of the alcohol, dissolves the residue in water and acidulates slightly (so that the fatty acids just commence to separate), renders slightly alkaline with sodium carbonate, and heats to boiling after adding some wool. Dimethyl-amidoazobenzene cannot be detected by the dyeing test ; its presence must be proved spectroscopically, after the colouring matter has been extracted from the soap solution by means of petroleum ether. It should be noted also that annatto dyes wool yellow.

Further notes on colouring matters will be found, Vol. III. Chap. XV., under the heading " Edible Fats."

Butter colours are similarly examined, using, of course, a smaller quantity of the sample. About 5 grms. are dissolved in 20-25 c.c. of petroleum ether, and treated with 10 c.c. of a 4 per cent solution of

[1] *United States Dept. Agric. Bureau of Chem.*, 1911, No. 63, p. 1.
[2] *Analyst*, 1912, 339.
[3] Second annual report of the Dairy and Food Commissioner of Pennsylvania.
[4] *Journ. Amer. Chem. Soc.*, 1898, 110.
[5] Crompton and Simonds, *Journ. Amer. Chem. Soc.*, 1905, 270.
[6] *Chem. Centralbl.*, 1898, ii. 943.

potash.[1] *Reinsch*[2] states that a butter colour he examined contained 33 per cent mineral oil.

In commerce butter is not merely valued by its purity (as ascertained by the tests described in the foregoing lines, and the chemical tests for butter fat to be described below), but its value depends also to a considerable extent on its flavour and taste. A proper valuation of butter on the strength of the last two properties hardly belongs to the province of the analytical chemist, as it requires a good deal of practice, which is not based on chemical evidence.

Different countries and even different provinces of one and the same country require differently flavoured butters; and their value is judged regularly in commerce without having recourse to chemical analysis.

In this connection it may be pointed out that the peculiar aroma of a good butter is due to the action of a bacterium, which gives rise to the formation of the flavouring substance during the ripening of the cream. That this is the case is shown by the general experience that the desired butter aroma does not appear in sweet cream butter prepared without the addition of a "*starter*," such butter having what is termed a "flat" (insipid) taste. A bacterium of this kind, to the presence of which the flavouring of ripened cream could be attributed, was first isolated by *Storch*. *Weigmann*[3] described two forms or races, one of which develops an exquisite flavour and aroma, but yields a butter which does not keep well, whilst the second race develops less aroma, but the butter keeps better. The cultivation of cream-ripening bacteria has been considerably advanced in America by *H. W. Conn.*[4] Laboratory experiments having demonstrated that a particular butter bacillus can produce a pleasant flavour, if inoculated into the cream during the process of ripening under such conditions that it can grow rapidly, pure cultures of this bacillus were distributed amongst numerous dairies. By this means the "June flavour," which had hitherto only been met with in butter of certain districts during a short season of the year, can now be produced artificially. This flavour is stated to be retained in the butter even for a longer period than the flavour which is obtained without such aid in ripening. In addition to the fine flavour a somewhat enhanced keeping property is said to be imparted to the butter.[5] An artificial flavouring compound consisting of sesamé oil with the addition of amylacetate and coumarin

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[1] The following formulæ for butter colours have been quoted by *Leffman* from a *Druggist's Circular* :—

Extract of Annatto	.	10 ounces.		Annatto seed, bruised	.	10 parts.
Turmeric	. . .	5 ,,		Turmeric	. . .	3 ,,
Logwood chips	.	2½ ,,		Ammonium carbonate	.	1 part.
Cotton seed oil	.	1 gallon.		Cotton seed oil	. .	75 parts.
				Lard	. . . .	10 ,,

[2] *Chem. Centralbl.*, 1912 (1), 1130.
[3] *Milchzeitung*, 1896, 793.
[4] Cp. *Agricultural Bacteriology*, London, 1909, Rebman, Ltd.
[5] Rosengren, *Milchw. Zentr.*, 1912, 321 ; cp. also Weigmann and Wolff, *ibid.*, 1912, 529.

is sometimes added to butter. Another method, due to *Müller*,[1] consists in adding 2-5 per cent of lecithin to the sweet cream and allowing it to ripen for 30 hours at 12-15° C.

In order to increase naturally the proportion of lecithin in cream *Witte*[2] pasteurises the cream, cools it quickly to 2-4° C., and keeps it at that temperature for from 1 to 10 days. It is then raised to from 16 to 30° C., soured, and allowed to mature.

" Fishy " butter is met with in Norway, being obtained from cows fed on fish meal.

Badly flavoured colonial butter has also been termed " fishy " butter or butter suffering from " fishiness." This is stated to have been caused by the contact of the milk or cream with rusty utensils or with copper. Others have ascribed this defect to the action of a micro-organism acting on the proteins in butter.[3] The growth of this organism is said to be prevented by " salting " the butter or by cold storage. Another kind of " fishy " butter is represented by overworked renovated butter.

" Sandy " butter (which contains undissolved salt granules), and other kinds of butter having an objectionable flavour will naturally be either rejected or must be sold at low prices. *Stocklin and Crochtelle*[4] state that the milk obtained from cows which have been fed on cakes derived from cruciferous plants contains sulphocyanides. This stands in need of confirmation. Most of the badly flavoured butters,[5] as also those which are mouldy, spotty,[6] discoloured, etc., are re-worked and sold as renovated butter.

Rogers and Gray[7] state that butter prepared from acid cream develops an unpleasant flavour on keeping even at -10° F.

" **Renovated** " butter or " **process** " butter (French — *beurre renové, beurre rebroyé* ; German,—*Aufgefrischte Butter, Renovierte Butter*) is manufactured in large quantities in the United States (since 1883). It is stated that during 1902 the production of " process " butter amounted to 5,879,833 lbs., equal to about half the quantity of margarine (" oleomargarine ") made in the United States. It is manufactured from unsaleable, " rancid " butter[8] by melting and separating the butter fat from the aqueous solution and the curd. The fat is next blown with air to remove the objectionable flavour, and then quickly cooled in a current of cold water so as to prevent the separation of the more liquid portion of the butter (" butter oil ") from the more solid portion. The butter fat is then churned with fresh milk, to which cultures of suitable bacteria have been added. The milk soon becomes

[1] German patent 221,698.
[2] English patent 1744, 1910.
[3] L. A. Rogers and C. E. Gray, *United States Dept. Agric.*, 1909, 114.
[4] *Chem. Zeit.*, 1910, 695.
[5] Cp. H. Weigmann, *Landw. Jahrb.*, 1908 (37), 261.
[6] The appearance of spots ("marbled butter") seems to be due to the defective removal of buttermilk, or to the fact that the salt has not been evenly distributed in the butter.
[7] *United States Dept. Agric.*, 1909, No. 119.
[8] J. Oudsteyn, United States patent 1,042,471 ; American Farm Products Co. English patent 7500, 1907 ; Higgins, English patent 15,221, 1913.

sour and coagulates, thus furnishing an artificial curd containing about the same proportions of nitrogen as does the curd of genuine butter. It is evident that by chemical methods alone "renovated butter" cannot be distinguished from genuine butter, the fat contained in such butter being of course genuine butter fat, and the proportions of the constituents being as a rule so regulated as to simulate the composition of a normal butter. This is exemplified by the mean of seventy-five analyses of process butters published by *Crampton* [1] :—

	Maximum.	Minimum.	Mean Value.
	Per cent.	Per cent.	Per cent
Fat . . .	88·88	68·80	82·05
Curd . . .	2·65	0·77	1·47
Ash . . .	7·49	0·97	2·85
Water . .	23·17	8·01	14·44

" Process or renovated butter " is defined by the " Act of Congress of 9th May 1902 " as butter which has been subjected to any process by which it is melted, clarified, or refined, and made to resemble genuine butter. Process butter containing any substances foreign to butter or more than 16 per cent of water is classed as " adulterated butter."

Hess and Doolittle [2] propose to identify renovated butter by the appearance of the curd, as the curd from process butter is milk-casein, whereas the curd from normal butter is the protein of cream. They further state that renovated butter presents under a polarisation microscope a different appearance from genuine butter. In genuine butter the fat is contained in isotropic, or at any rate in such micro-crystalline form that under the polarisation microscope with moderate magnification no polarising crystals, or at any rate only few, are noticed. Renovated butter shows, on the contrary (like margarine), throughout the whole mass a distinct crystalline structure.[3] For the details the reader must be referred to the original paper, and it need only be added that, according to *Hess and Doolittle*, " process butter " does not yield a clear layer of fat on melting, even after some prolonged standing, whereas the fat of pure butter becomes clear soon after melting. This may explain the observation that renovated butter (like margarine) is characterised by " spurting " when heated in a pan, whereas genuine butter froths quietly.

Renovated butter does not keep as well as genuine butter, and, owing to the large amount of air incorporated with it, it is prone to acquire a " fishy " taste.

The production of renovated butter must be carried out with

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[1] *Journ. Amer. Chem. Soc.*, 1903, 358.   [2] *Ibid.*, 1900, 150.

[3] Cp. Bomer, *Zeits. f. Unters. d. Nahrgs. u. Genussm.*, 1908 (xvi.), 27. Fincke, *ibid.*, 1908 (xvi.), 670, goes even so far as to state that normal *Reichert-Meissl* value, normal titration numbers of the insoluble volatile acids, and normal saponification value only speak in favour of the genuineness of a butter fat, if the examination under the polarisation microscope has proved the absence of crystalline glycerides from the melted state.

scrupulous cleanliness throughout. The renovated butter works which the author saw in the United States were equipped in an entirely unobjectionable manner. It appears that the production of renovated butter is being adopted in Europe, and several patents for " renovating " have been taken out during recent years.[1]

Siberian and Danish butters in particular appear to be used in Germany for the production of renovated butter, as they suffer in transit and the outer portions become rancid.[2] These outer rancid portions are scraped off and sold as inferior butter (" Kratzbutter," " Staff "), or treated for renovated butter. Butter refined in Germany by treating a rancid butter with " Neutroxyd " [3] must be considered a " renovated " butter.

Renovated butter is now being admixed (fraudulently) in Germany with fresh butter. The detection of an admixture of renovated to fresh butter is a problem which, in the present state of our knowledge, cannot be solved by chemical means.

The presence of curd and water renders butter far more liable to become rancid than is the case with pure butter fat. Hence in some countries, as in South-West Germany, India (known as " Ghee " or " Ghi "), Siberia (for export to Turkey)—in Egypt the word " Samna " denotes the same fat—butter is melted until the butter fat has become quite clear, whereupon the latter is separated from the curd and water. The flavour of such butter (" Schmelzbutter ") suffers, however, considerably.

A sample of native butter fat (Samli) from Wilhelmstal, German East Africa, on examination by *Thoms* [4] showed the following composition :—

	Per cent.
Moisture (water content) . . .	0·665
Casein and milk sugar	1·929
Mineral parts	0·01
Fat content	97·396

The fat, after separation from the albuminoids had the following characteristics :—

Solidifying point, ° C.	24
Melting point, ° C.	36-37
Saponification value	224·13
Iodine value	31·6
Acid value	17·94
Refractometer value at 40, ° C. . .	42
Reichert-Meissl value	26·87
Polenske value	2·24

The taste was extremely rancid.

[1] Belgian patent 172,592 ; English patent 28,374, 1904 ; French patent 355,362 ; English patent 7500, 1907 ; English patent 28,024, 1907 ; United States patent 881,929 (W. F. Jensen) ; French patent 396,282 (M. Montéran).
[2] Cp. Geock, *Zeitschr. f. öffentl. Chem.*, 1908, 198.
[3] This consists of a mixture of magnesium carbonate and magnesium silicate.
[4] *Chem. Revue*, 1914, 56.

If the temperature employed in melting the butter is too low, the separation of the water and casein does not take place completely, and hence the butter is liable to become rancid. On the other hand, if the temperature in melting be too high, the butter fat acquires a tallowy taste.[1]

The literature dealing with the rancidity of butter is a very voluminous one, but, unfortunately, a number of writers seem to have confounded butter fat with butter. The conditions influencing the liability of butter fat to become rancid have been fully explained in Vol. I. Chap. I. Although the determination of the free fatty acids in butter fat (acid value of the butter fat) is of little use, since acidity is not coterminous with rancidity, it is still the practice of some analysts to determine the amount of free fatty acids in butter fat in order to arrive at a " measure of rancidity." If a measure of the amount of hydrolysis which a butter fat has suffered be desired, the determination of the acetyl value—indicating in this case the amount of mono- and di-glycerides—will afford the required information. Two samples of rancid butter fat twenty-two years old showed on examination normal figures for the iodine value, Reichert-Meissl value, and insoluble volatile acids. Formic acid could not be detected.[2]

The conditions favouring the rancidity of butter fall outside the scope of this work, and the reader must therefore be referred to the original papers given in the footnote.[3]

The paper in which the butter is wrapped has an important bearing on the keeping qualities of butter.[4]

On exposure to light butter not only loses its yellow colour but also acquires a tallowy (" lardy ") smell and taste.

II. Examination of the Butter Fat

For tables of characteristics see pp. 804-806.

For characteristics of the milk fats from other animals than cows see p. 807.

Pure butter fat consists almost exclusively of triglycerides of fatty acids. Besides triglycerides it contains cholesterol and some natural colouring matters (lactochromes). The total amount of unsaponifiable

[1] Laxa, Milchw. Zentr., 1912, 673. Cp. also Worrall, United States patent 1,045,926.
[2] Sebelien, Landw. Versuchsst., 1913, 389.
[3] Schmidt, Zeits. f. Hygiene. u. Infectionskrankheiten, 1898, 163 ; Hanus, Zeits. f. Unters. d. Nahrgs.- u. Genussm., 1900, 324 ; Hanus and Stocky, ibid., 606 ; Lydia Rabinowitsch, Jahrbuch d. Chem., 1899, ix. 237 ; Crampton, Journ. Amer. Chem. Soc., 1902, 711 ; Orla Jensen, Jahrbuch d. Chem., 1902, xii. 363 ; O. Laxa, Arch. f. Hygiene, 1902, 119 ; A. Nestrelajew, Zeits. f. Unters. d. Nahrgs.- u. Genussm., 1911, 431 ; M. Siegfeld, Milchw. Zentralbl., 1908, 530.
[4] Ferenczi, Zeits. f. angew. Chem., 1911, 2241 ; Schacht, Analyst, 1911, 597 ; Burr, Wolff, and Berberich, Zeits. f. Unters. d. Nahrgs.- u. Genussm., p. 200.

matter is less than a half per cent (0·35 per cent, *Bömer*; 0·31-0·41 per cent, *Lewkowitsch*; 0·42 per cent, *Klein and Kirsten*; [1] 0·215-0·325 per cent, *Siegfeld*). Lecithin has been stated by various observers to occur in butter fat to the extent of 0·017 or even 0·15 to 0·17 per cent (calculated from phosphoric acid). *Wrampelmeyer* [2] stated 0·007 to 0·033 per cent of lecithin. *Jaeckle*, however, showed that butter fat contains no compound of phosphorus.

The following acids have been identified hitherto in butter fat :— acetic,[3] butyric, caproic, caprylic, capric, lauric, myristic, palmitic, stearic, arachidic, and oleic. *Wachtel*, as also *Bondzyński and Rufi*, stated that butter fat contains hydroxylated acids, and on the strength of their results, obtained by the application of faulty methods, *Browne* [4] has even gone so far as to calculate the percentage of hydroxylated acids. Experiments made by the author prove, however, that butter fat contains practically no hydroxylated acids, the low acetyl values found being due to the presence of small quantities of mono- and di-glycerides.

The extraordinarily high percentage of glycerides of soluble fatty acids in butter fat is characteristic, and differentiates it from all other fats.[5] Especially characteristic of butter fat is the presence of butyric acid (which is absent from cocoa nut and palm nut oil).

The quantity of stearic acid obtained by the method described in Vol. I. Chap. VIII. is very small. In an analysis carried out in the author's laboratory with a sample of butter fat of the *Reichert-Meissl*

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[1] *Zeits. f. Unters. d. Nahrgs.· u. Genussm.*, 1903, 147.

[2] *Landw. Versuchsst.*, 1903, 437.

[3] Cp. E. Wein, *Inaug. Dissert.*, Erlangen, 1876. The statement, however, requires confirmation. Wein claims also to have detected the presence of formic acid in fresh butter fat.

[4] *Journ. Amer. Chem. Soc.*, 1899, 613.

[5] Buttenberg (*Zeits. f. Unters. d. Nahrgs.· u. Genussm.*, 1908, 335) describes a peculiar vegetable oil, said to be obtained from a Chinese seed, which has a remarkably high *Reichert-Meissl* value, viz. 34·85. The examination of this oil, which Buttenberg obtained from Holland under the name "Butter Oil" (!), had the following characteristics :—

Saponification value	284·7
Reichert-Meissl value	34·85
Titration number of the insoluble volatile acids .	0·55
Iodine value	64·6
Unsaponifiable matter	0·38 per cent.

Melting point of the eighth crop of crystals from unsaponifiable matter, 179·6-180·6° C.
Melting point of the alcohol recovered from the acetate, 163 7-166·2° C.
The "alcohol" melted after recrystallisation from ethyl alcohol at 177·3 to 178·3° C., and showed under the microscope the characteristic crystal form of phytosterol.
The oil did not give the *Halphen* reaction (for cotton seed oil), but gave positive colour reaction for sesamé oil, although only faintly.
These numbers suggested to me the conjecture that this new oil is an artificially prepared mixture of vegetable oils (containing sesamé oil) with butyrin or caproin, designed to serve as a butter adulterant. Buttenberg, however (in a private communication to me), declared that there was no reason to doubt that the new oil was a natural one. The presence of butyrin or caproin can be easily ascertained ; the melting point of the "alcohol" and its "acetate" in the unsaponifiable matter appear, however, peculiar.
An oil remarkable for a still higher *Reichert-Meissl* value—viz. 35·31—is spindle-tree oil from the seeds of *Evonymus europaea*, L., p. 226.

value 28·1 the· amount of stearic acid found in the insoluble fatty acids was only 0·49 per cent (see Vol. I. Chap. XII.). The presence of less saturated acids than oleic acid in a normal butter has not yet been proved beyond doubt. *Färnsteiner* has shown that, in the butter from a đow fed on cotton meal, traces of linolenic acids were ascertainable. *Partheil and Ferié* stated that less saturated acids than oleic occur in butter fat to a somewhat considerable extent; but, as the method by which their presence was determined is not free from serious objections (Vol. I. Chap. VIII.), their statement must be accepted with reserve.

According to *Duclaux*,[1] butter fat contains from 2 to 2·26 per cent of caproic, and from 3·38 to 3·65 per cent of butyric acid. From this he (somewhat arbitrarily) assumes the proportion in which butyric acid stands to caproic in butter fat to be 1 : 1·645.

On this basis *Violette* [2] calculated severally the proportions of butyric, caproic, solid volatile, and insoluble fatty acids by proceeding in the following manner :—50 grms. of butter fat are saponified and the volatile acids separated, as in *Reichert's* distillation process. The solid, volatile acids are separated by filtration, and their quantity determined after drying ; [3] the amount of the insoluble fatty acids is arrived at in the same way. The total quantity of the soluble acids is ascertained by titration with decinormal alkali, and calculated to butyric acid. If A represent this quantity, then the quantities of butyric and caproic acids, B and C, can be calculated on the above-stated assumption with the help of the following equations :—

$$B = A \times 0.68469$$
$$C = A \times 0.41565$$
$$\frac{B}{C} \text{ being} = 1.645.$$

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[1] *Compt. rend.*, 1886 (102), 1022.   [2] *Journ. Soc. Chem. Ind.*, 1890, 1157.
[3] With regard to errors caused by this procedure cp. Vol. I. Chap. VIII.

Physical and Chemical Characteristics of Butter Fat

Specific Gravity		Solidifying Point		Melting Point [2]		Saponification Value		Iodine Value	
°C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	Hager	19·20	Wimmel	29·5-34·7	Bell	227	Kottstorfer,	26·0-35·1 [5]	Hübl
37·8 (100° F.) (water 37·8 = 1)	Bell	20·23	Thorner	29·4-33·3	Cameron	(221·5-233·4)	Valenta, Moore,	25·7-37·9 [5]	Wollny
,, 40	Thorpe			28-33	Thorner		Allen, etc.	29·0-43	O. Jensen
(water at 15·5 = 1) 100	Allen					225-230	Thorner	30·6-50·3	van Rijn
(water at 15·5 = 1) 100	Koenigs					221-233	Seyda and Woy [3]		
(water at 15·5 = 1) 100	Allen					219·7-232·6	Thorpe [4]		
(water at 100 = 1) 100	Wolkenhaar					(Cp. p. 713)	K Fischer		
,,	Bell								
,,	Muter								
	Allen								
15	Salomone [1]	19·1-24·5	Salomone	29·7-32·7	Salomone	209·3-237·1	Salomone	29·8-37·5	Salomone

Specific Gravity values: 0·936-0·940, 0·911-0·913, 0·916-0·918, 0·1041, 0·865-0·868, 0·867-0·870, 0·901-0·904, 0·9094-0·9140, 0·9105-0·9138, 0·9099-0·9132, 0·9358-0·9443

[1] 5 samples from Tripoli and Cyrena. *Boll. Chim. Pharm.* (52), 465.

[2] According to Meyer (*Milch-Zeit.* 1892, 49) the melting point of cow butter is lowered by food consisting of easily digestible carbohydrates, but raised by straw, oil cakes, or sour fodder.

[3] Silesian butters. [4] Calculated by me from the "saponification equivalents" of 857 English butters. [5] 56 samples, mean 33·32.

Physical and Chemical Characteristics of Butter Fat—continued

Reichert Value.

c.c. $\frac{1}{10}$ norm. KOH.	Observer
14 (12.5-15.2)	Reichert, Moore, Allen, etc.

Reichert-Meissl Value.

20.63-38.15	Cp.rp. 823-825 Salomone
21.6-33.2	

Thermal Test.

Heat of Bromination.

°C.	Observer
5.6-7.0	Hebner and Mitchell
9.5	Broomwell and J. L. Meyer

Refractive Index.

At °C.		Observer
25	1.4590-1.4620	Wollny
60	1.445-1.448	Thorner

Oleo-refractometer.

"Degrees." At 45° C.	Observer
−29 to −31	Jean
−25 to −31	Pearmain

Butyro-refractometer.

At °O.	Scale Divisions.	Observer
25	52.5	Skalwelt
25	49.5-54	Wollny
35	44.8-47	Besana
40	41-42	Mansfeld
40	40.5	Beckurts and Seller
40	40.5-44	Delaite
45	37.6-42.5	Thorpe
45	38.9-45.5	van Rijn
40	37.5-40.6	Salomone

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Insoluble Acids + Unsaponifiable.		Specific Gravity.		Solidifying Point.		Melting Point.[1]	
Per cent.	Observer.	At 37·75° C. (water 15·5° C.=1).	Observer.	°C.	Observer.	°C.	Observer.
87·5	Hehner	0·9075-0·9085	Leonard	35·8	Hübl	38	Hübl
86·45-89·8	Bell	0·90919-0·91357	Bell	37·5-38	Paris Municipal Laboratory	41·43 and 43·45	Bensemann
				33-35	Thörner	38-40	Thörner

Physical and Chemical Characteristics of the Insoluble Fatty Acids—continued

Neutralisation Value.[2]		Iodine Value.		Heat of Bromination.		Refractive Index.	
Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At 60° C.	Observer.
210-220	Thörner	28-31	Thörner	6·2	Hehner and Mitchell	1·437-1·439	Thörner

[1] Butter from cows fed on cotton seed cakes has a considerably (by 8° to 9° C.) higher melting point (Lupton, *Journ. Amer. Chem. Soc.*, 1891, 134).

[2] The neutralisation values of the fatty acids obtained after distilling off the volatile fatty acids by Reichert's process were found 213·3 to 218·9 (Henriques).

Characteristics of the Milk Fats from other Animals

Milk fat from	Specific Gravity At 15° C.	Specific Gravity At 100° C.	Solidifying Point	Melting Point	Saponification Value	Iodine Value	Reichert-Meissl Value	Insoluble Acids + Unsaponifiable	Refractive Index	Unsaponifiable Matter Per Cent.	Observer
Goat [1]	0.9312	0.8669	24.31	27-38.5	221.6	30.4-34.6	23.1-25.4	86.5-87.3	1.4596		Solberg
,,		0.8651	31	36.5			28.6				Pizzi
,,					233.9-241.8	21.1-28.7	21.1-24.3				K. Fischer [2]
,,		0.8637			226.1-242.4	25.2-38.9	17.2-29.1	87.8			Sprinkmeyer and Furstenberg [3]
"Egyptian"					235.-15	24.7-33	20.6-26.5		40.7-43.6 ("Degrees")[5]		Paraschtschuk [4]
					224.5-232.0		20.8-22.9.4				Lucas [1]
Sheep				29-30	235.1-237.1	30.2-32.7	32.9				Pizzi
,,					216.6-228.2		28.8-32.3				Don [6]
,,							22.9-26.5.7		44.0 ("Degrees")[5]		Lucas
"Egyptian"							11.2				Pizzi
Ass [8]							13.1				,,
,,							26.2				
Buffalo (Bulgarian)		0.8692	29	38	229.0	36.75	34.2	88.19	44.5 ("Degrees")[5]		Petkow [9]
Buffalo (Indian)		0.8965			206.8		18.24	90.65	42.0	0.73	Menon [10]
Buffalo (Egyptian)					228.?		32.3		42.0 ("Degrees")[5]		Lucas [11]
Reindeer		0.8640	34-39	37-42	219.2	25.1	31.4	86-89	("Degrees")[5] 1.4647		Solberg
Gamoose (Buffalo)	0.9428				220.4-231.7	32.35	34.7-35	86.9-87.5	Oleo-refractometer. "Degrees."		H. D. Richmond
Camel		0.870		≈38 [12]	209	55.1	15.8 [14]	89.2	-20		Vamvakas [12]
Woman					218.4	43.4				4.68 [14]	Sauvaitre [15]

[1] Milchw. Zentralbl., 1907, 507.
[2] Zeits. f. Unters. d. Nahrgs.- u. Genussm., 1908 (xv.), 12. Butyro-refractometer 36.5-41.0 "degrees" at 40° C. Titration number of insoluble volatile acids 6.85-9.80. Mean molecular weight of the non-volatile acids 253.6-269.3. Butyro-refractometer of these acids 28-33.1 "degrees" at 40° C.
[3] Zeits. f. Unters. d. Nahrgs.- u. Genussm., 1907, xiv. 390; 1908, xv. 413. Butyro-refractometer at 40° C. 40.4-43.8 "degrees." Titration number of in-soluble volatile acids (see p. 839) 3.15-8.00. Mean molecular weight of non-volatile fatty acids 244.5-266.5. Butyro-refractometer of these non-volatile acids 29.2-33 "degrees" at 40° C. Cp. also Dons, Zeits. f. Unters. d. Nahrgs.- u. Genussm., 1908, xv. 73.
[4] Insoluble volatile 4.9-6.5.
[5] Butyro-refractometer at 40° C. Titration number of

insoluble volatile acids (see p. 839) 5.2-6.6. Butyro-refractometer at 40° C. 38.2-38.9 "degrees."
[7] Insoluble volatile 2.8-3.1.
[8] The proportion of fat in the milk varies, according to Wagner, from 8.1 to 0.1 per cent, and even less (Zeits. f. Unters. d. Nahrgs.- u. Genussm., 1906, xii. 659; 1908, xvi. 175).
[9] Zeits. f. Unters. d. Nahrgs.- u. Genussm., 1901, 826.
[10] Journ. Soc. Chem. Ind., 1910. The titer test of the insoluble fatty acids was 45.3, and the mean molecular weight and iodine value 273.8 and 30.7 respectively.
[11] Cairo Scientific Journ., 1911, 308. Insoluble volatile acids, KOH. rh = 1.6 c.c.
[12] Chem. Centralbl., 1905, ii. 1130; Analyst, 1905, 370.
[13] Chem. Centralbl., 1905, ii. 1130; Analyst, 1905, 370.
[14] Total volatile acids 4.41 per cent. Ratio of butyric acid to caproic acid 2.4 : 1. A normal cow butter gave to Sauvaitre 1.58 per cent of unsaponifiable matter.
[15] Ann. Chim. Analyt., 1902, 143. Cp. also A. Joles, Chem. Zeit., 1908, 505.

In the following table *Violette's* results are reproduced :—

Fatty Acids.	Superior Qualities of Butter.			Inferior Qualities of Butter.				
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Butyric acid .	6·07	5·33	5·50	5·05	4·62	4·80	4 76	4·37
Caproic acid .	3·66	3·23	3·34	3·06	2·80	2·92	2·89	2·65
Solid volatile acids	2·85	3·00	2·80	3·00	2·90	2·40	3·00	2·95
Non-volatile acids .	82·28	82·63	82·87	83·20	84·32	84·31	83·83	84·62
Total . .	94·76	94·19	91 41	94·31	94·64	94·43	94·48	94·59

By ascertaining finally the mean molecular weights of the solid volatile and of the non-volatile acids, *Violette* obtained all the data necessary for calculating the composition of the butter fats. This is given in the following table :—

Glycerides.	Superior Qualities of Butter.			Inferior Qualities of Butter.				
	I	II.	III	IV.	V.	VI	VII.	VIII.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent	Per cent.	Per cent.
Butyrin . . .	6·94	6·09	6·28	5·76	5·28	5·49	5·45	5·00
Caproin . . .	4·06	3·58	3·70	3·39	3·09	3 23	3·10	2·94
Glycerides of solid volatile acids . .	3·06	3·22	2·96	3·16	3·06	2·53	3·16	3·15
Glycerides of non-volatile acids . .	85·98	86·62	86 60	86·93	88·10	88·10	87·60	88·42
Difference . .	0·04	0·49	0·46	0·76	0·47	0·65	0·69	0·49
	100	100	100	100	100	100	100	100

Subjoined is a table showing the composition of butter fat, calculated by the author from the data given by the observers named :—

Glycerides.	J. Bell.	W. Blyth.	Spallanzani [1]
	Per cent.	Per cent.	Per cent.
Butyrin· . . .	7·012	7·7	5·080
Caproin . . .	} 2·280	0·1	{ 1·020
Caprylin and caprin .			0·307
Olein . . .	37·730	42·2	} 93·593
Palmitin, stearin, etc. .	52·978	50·0	
	100	100	100

[1] *Le Staz. Sperim. Ital.* (1890), 23, 417.

How the theoretical composition of a butter fat may be calculated from the numbers obtained on examining it by the quantitative tests, has been shown above (Vol. I. Chap. XI.). In the example given there the volatile fatty acids were found by difference; the volatile acids may be further resolved into soluble volatile and insoluble volatile acids (*Violette's* solid volatile acids; cp. *Muntz and Couden's* as also *Polenske's* methods, p. 839). The calculated mean molecular weight of the mixed volatile acids was 114. In the example, given Chap. XII., stearic acid was determined direct; the sum of all other saturated fatty acids was obtained by difference.[1]

Muntz and Coudon[2] gave as the total amount of *soluble volatile acids*, expressed as butyric acid, the following percentages :—

Rich butter	6·50 per cent	
Medium butter	5·50	,,
Poor butter	5·25	,,
Very poor butter	5 00	,,
Exceptionally poor butter	4·90	,,

It should be noted that the quality of the butter is judged here by the percentage of soluble volatile acids; this factor would not be recognised in commerce as the guiding principle, since the flavour and taste of a butter, and hence its commercial value, do not depend exclusively on the larger or smaller amount of soluble volatile acids, which only chemical analysis reveals. The amount of *insoluble volatile acids*, also expressed in terms of butyric acid, was found by *Muntz and Coudon* in two butters to lie between 1·74 per cent and 1·96 per cent.

Muntz and Coudon give for the relation (see p. 832)—

$\dfrac{\text{Insoluble volatile acids}}{\text{Soluble volatile acids}} \times 100$, the mean number 12·04, the minimum being 9·1 and the maximum 15·6 (cp. also below, p. 836).

From the foregoing numbers it will be gathered that butter fat is distinguished from all other fats by its high proportion of butyric acid.

The mean molecular weights of the soluble volatile acids of butter fats, having the *Reichert-Meissl* values 26·3-27·5, were stated by (*Juckenack and Pasternack*[3] to be 95·1-98·3. *W. Arnold*[4] gives 98 as an average; *Siegfeld* 98·4-103. These figures refer to the volatile acids as obtained in the 110 c.c. distillate from 5 grms. of butter fat in the *Reichert-Meissl* (*Reichert-Wollny*) test. The number 98 proves clearly that besides butyric acid some higher volatile acid or acids are dissolved in the aqueous solution of the volatile acids.

The mean molecular weight of the *insoluble volatile acids* has been given by *Siegfeld* as lying between 177 and 207; but, as he himself points out, the method by which these mean molecular weights have

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[1] Cp. also Fleischmann and Warmbold, *Zeits. f. Biologie* (1907), 4, 375. Siegfeld, *Milchw. Zentralbl.*, 1907, 288; *Chem. Zeit.*, 1908, 505.

[2] *Annales de l'Institut National Agronomique*, Paris, 1904.

[3] *Zeits. f. Unters. d. Nahrgs.- u. Genussm.*, 1904, 1204.

[4] *Ibid.*, 1905, 841.

been determined is so inaccurate that no reliance can be placed on those figures.

The mean molecular weights of the *insoluble acids* fluctuate between 258 and 266, the lowest number being, of course, due to a fat having the highest *Reichert* value and the highest being due to a fat having the lowest *Reichert* value. It may, however, be pointed out already here that the conclusions which various observers have attempted to draw from the mean molecular weight of the insoluble fatty acids as to the composition of the (nearly) 94 per cent of insoluble fatty acids are hardly valid. For any number of mixtures of fatty acids from lauric upwards to arachidic can be present in butter fat, all having mean molecular weights from 258 to 262.[1] An investigation which the author has undertaken shows that some butters are richer in arachidic acid than others, which, on the other hand, seem to contain larger amounts of myristic acid. It is to be hoped that a closer study of the insoluble acids will lead to a more intimate knowledge of the composition of butter fat, and will incidentally furnish analytical means to reveal adulterations of butter, which hitherto escape detection. For most of the usual methods in vogue deal with the volatile acids only, without taking any detailed notice of the composition of the insoluble acids. The lithium-salt method of *Partheil and Ferié,* which was stated to be capable of resolving the insoluble fatty acids into their several components, viz. lauric, myristic, palmitic, and stearic acids, has been shown to be unreliable (Vol. I. Chap. VIII.). Hence the detailed analysis of a butter by those chemists given in the third English edition of this work is not reproduced here.

On reducing a butter fat of the iodine value 37 with colloidal palladium, Vol. I. p. 59, *Paal and Roth* [2] obtained a hard white fat softening at 36° C. and melting at 44° C. The iodine value was nil. The fat had a pleasant nutty taste somewhat resembling cacao butter.

On treating butter fat with 95 per cent alcohol in the same manner as described under "Lard" (p. 700) glycerides richer in olein pass into the alcoholic solution. The characteristics (1) of the original fat, (2) of the alcohol-soluble portion, (3) of the alcohol-insoluble portion are collated in the following table (*Arnold* [3]) :—

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[1] Vol. I. Chap. VIII.   [2] *Berichte*, 1909, 1551.
[3] *Zeits. f. Unters. d. Nahrgs.- u. Genussm.*, 1907, xiv. 194 ; cp. *ibid.*, 1908, xvi. 666.

| | Butyro-refractometer at 40° C. "Degrees." | Saponification Value. | Reichert-Meissl Value. | Mean Molecular Weight of the Soluble Volatile Acids. | c.c. n/10 KOH required for Insoluble Volatile Acids (Polenske's Method). | Iodine Value | Non-volatile Fatty Acids. | | | Yield of Alcohol-soluble Portion (from 150 grms. of fat). |
							Butyro-refractometer at 40° C. "Degrees."	Neutralisation Value.	Iodine Value.	
1. Original fat	43·7	223·5	25·0	101·4	2·1	42 6	32·4	214·5	45·7	Grms. ...
2. Alcohol-soluble fat .	40·1	229·9	36·1	100·1	2 70	45·0	34·0	124·0	50·2	36·09
3. Alcohol-insoluble fat	44·3	220·1	21·2	103·1	1·75	41·2	32·0	214·0	43·0	...

It appears very likely that the bulk of the triglycerides in butter fat are "mixed" glycerides. The opinion that mixed glycerides occur in butter fat was first pronounced (before oleo-distearin was isolated) by *J. Bell*,[1] on the strength of experiments made by *G. Lewin* in the Government Laboratory. *Bell* stated that a mixed glyceride of the following composition occurs in butter fat :—

$$C_3H_5 \begin{cases} O.C_4H_7O \\ O.C_{16}H_{31}O \\ O.C_{18}H_{33}O. \end{cases}$$
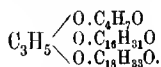
The following facts support this opinion : If ordinary animal fat is melted and mixed with—say 10 per cent of—butyrin, the latter may be entirely removed by digestion with alcohol,[2] the animal fat being recovered practically in its original condition. If, however, butter fat is treated with hot alcohol, from 2 to 5 per cent only of its weight remains dissolved in the alcohol after cooling to the ordinary temperature. The fat thus dissolved does not consist of butyrin or caproin,. but of a glyceride which is liquid at 15·5° C., and yields on saponification from 13 to 14 per cent of soluble fatty acids, and from 79 to 80 per cent of insoluble fatty acids. The latter have a higher melting point than the mixed insoluble acids obtained from the orginal butter fat ; this tends to disprove the opinion that the low melting point of the extracted fat might be due to an increased proportion of oleic acid in the molecule. These results agree closely with a compound of the above given formula, which *Bell* named oleo-palmito-butyrate of glycerol.

A. W. Blyth and Robertson[3] stated that they isolated from butter fat a crystalline glyceride, to which they ascribe the formula

$$C_3H_5 \begin{cases} O.C_4H_7O \\ O.C_{16}H_{31}O \\ O.C_{18}H_{35}O, \end{cases}$$

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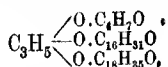
[1] *The Chemistry of Foods,* ii. 44.
[2] Cp. Fincke, *Zeits. f. Unters. d. Nahrgs.- u. Genussm.,* 1908, xvi. 673.
[3] *Proceed. Chem. Soc.,* 1889, 5.

but no great weight should be attached to this preliminary communication, which has not been followed up by detailed researches.

Further experiments are required to resolve the apparently very complex mixture of glycerides in butter fat into its component parts. In the present state of our knowledge the method of fractional crystallisation from solvents (cp. Vol. I. Chap. XII.) offers the best hope of success.

Caldwell and Hurtley[1] attempted to separate the glycerides by fractional distillation *in vacuo* : the following *Reichert-Meissl* values were obtained :—

	Butter. I.		Butter. II.		Butter. III.			
	Distillate R.-M. Value.	Residue R.-M. Value.	Distillate R.-M. Value.	Residue R.-M. Value.	Distillate		Residue	
					R.-M. Value.	Iodine Value.	R.-M. Value.	Iodine Value.
Up to 250° C. .	48·0	30·7	50·9	8·4	57·6	19·7	.	..
Distillate redistilled . .	73·6	28·9	67·1	24·9	78·0	..	45·8	..

In order to prepare butter fat for the subsequent examinations, the sample of butter is melted in a porcelain dish at a temperature of about 50° C., until the upper layer has become perfectly clear. The supernatant fat is then decanted through a filter in the water oven.

It has been pointed out already that the adulteration of butter is at present practically confined to the admixture of foreign fats with butter fat, since added substances of a non-fatty nature are easily detected.

In view of the fact that so many new methods for testing butter fat are being recommended, it should be emphasised that many chemists who publish new methods seem to overlook entirely the fact that there is not the slightest difficulty in distinguishing pure butter from margarine, or indeed from any other fat.[2]

Before the methods of fat analysis had reached the present state of completeness, margarine was very frequently sold—and is being sold to-day—fraudulently as butter.

At present butter adulteration is practised on a most extensive scale by the admixture, in comparatively small proportions to the total fat, of foreign vegetable and animal fats, such as lard (goose fat), cotton seed stearine, cocoa nut oil, palm nut oil, and chiefly margarine ("oleomargarine"). The last named fatty compound will be considered more fully under the heading of "Butter substitutes" in Chapter XV.

Recently there has been sold for the purposes of butter adulteration, especially in Germany, a mixed fat consisting of butter fat, oleo-

[1] *Journ. Chem. Soc.*, 1909, 856.　　　　[2] Cp. however, footnote, p. 802.

margarine, cocoa nut oil, and cotton seed oil. As large a quantity as 30 per cent of this mixture can be added to certain butters without being detected by the so-called " rapid methods " (refractive index, *Reichert-Meissl* value, insoluble volatile acid number, saponification value, iodine value, etc.). Since, however, the detection of vegetable oils, even down to 5 per cent or 3 per cent, has become comparatively easy (see below), the adulterators have substituted for the above-mentioned mixture oleomargarine or lard, or mixtures of both, churned up with water, without addition of a colouring matter — in short, a margarine consisting of animal fats only.

I append a few analyses of such butter adulterants :—

	I	II	III.
Reichert-Meissl value	6·79	0·3	0·2
Titration number of insoluble volatile acids	10·53		
Butyro-refractometer at 45°C. "Degrees"	42·17		46·1
Iodine value	23·49		
Saponification value . . .	..	197·3	197·0

Butter adulteration is practised on such extensive lines that legislation [1] has stepped in to protect the genuine article. In this country no butter-substitute, however small the proportion of foreign fat, may be sold without a distinct declaration as to its true nature.

The French " Margarine Law " of the 17th April 1897 prohibits the sale, etc. under the name of " butter " of any substances not made exclusively from milk or cream. The regulations under the Act of 1897 have been amended by the " Adulteration Law " of the 1st August 1905, which imposes severe penalties for (amongst other frauds) attempting to falsify the analytical procedures.

The latest " Margarine Law " in Germany, 1897, as also in Austria, 1901, enacts that a manufacturer of margarine is bound to admix with the oils and fats employed 10 per cent of sesamé oil, for the sake of " ear-marking " such butter, as the recognition of sesamé oil is easy by means of the *Baudouin* test. This Act has, however, not been able to prevent the continuation of adulteration, since the importation of foreign made margarine, in the preparation of which no sesamé oil has been used, cannot be prevented.

The Belgian law demands the addition of 5 per cent of sesamé oil and 0·2 per cent of dry potato starch (reckoned on the fatty matter in the margarine). It also forbids the sale of " abnormal " butter.[2]

[1] A. Lavalle, *Die Margarine Gesetzgebung*, Bremen, 1896.— *Report of the Departmental Committee on Butter*, London, 1904.

[2] The law defined as "abnormal" a butter, the fat of which showed at least two of the following characteristics :—Scale divisions in the butyro-refractometer (at 40°) higher than 41 " degrees " ; critical temperature of dissolution with alcohol of 99·1 per cent, a number exceeding 59° C. ; specific gravity at 100° C., below 0·864 ; Reichert-Meissl value, below 25 ; percentage of insoluble fatty acids, above 89·5 ; and saponification value, below 221.

The definition of the latter has been made still more strict in the Belgian "Margarine Law" of 1903, amended the 21st November 1904.

The new law defines a butter as abnormal in composition if its *Reichert-Meissl* value falls below 28, and if, in addition, it has one of the following characteristics : Butyro-refractometer, at 40° C., above 44 scale divisions (" degrees ") ; a critical temperature of dissolution (in alcohol of 91·1°, *Gay Lussac*) above 57° C. ; specific gravity at 100° C., below 0·865 (it should be noted here that, curiously enough, the law omits to state to what temperature of *water* the specific gravity refers ; undoubtedly the specific gravity of water refers to 15° C.) ; the percentage of " insoluble and solid fatty acids " above 88·5 per cent (by *Hehner's* method [1]) ; a saponification value below 222.

According to the latest " Adulteration Laws " of the United States butter must contain 82·5 per cent of butter fat and a small proportion of other milk constituents, and may be made with or without common salt, and with or without colouring matter. According to the Act of 9th May 1902 adulterated butter is defined as " a grade of butter produced by mixing, re-working, re-churning, in milk or cream, refining, or in any way producing a uniform, purified, or improved product from different lots or parcels of melted or unmelted butter or butter fat, in which any acid, alkali, chemical, or any substance whatever is introduced or used for the purpose or with the effect of deodorising or removing therefrom rancidity or any butter or butter fat with which there is mixed any substance foreign to butter, with intent or effect of cheapening in cost the product of any butter in the manufacture or manipulation of which any process or material is used with intent or effect of causing the absorption of abnormal quantities of water, milk, or cream."

An Act of Congress of the 1st July 1902 gives as one of the chemical standards for butter fat a *Reichert-Meissl* number not less than 24, and a specific gravity of not less than 0·905 at 40° C. (water at 40° C. = 1). It should, however, be mentioned here that there are separate Food Laws in the various States of North America which are not in conformity with this Act of Congress.

The Netherlands " Margarine Act " of 1900 defines butter as an article of no fat constituents other than those derived from milk. As this law has not been able to prevent adulteration, a number of farmers and dairy owners have privately combined to guarantee their butter as pure, and placed themselves under the supervision of " Control Stations." The Netherlands Government granted an official mark of guarantee in 1904 to seven Control Stations. Such butter is sold under the name " Dutch Control Butter." An Act, dated 17th June 1905, authorises the use of an official control mark which is issued by the Department of Agriculture.

The Dutch " Margarine Act " has been supplemented by the " Butter Act " of the 13th August 1908.[2]

The Danish " Margarine Law " of 22nd March 1897 punishes

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[1] This includes, of course, the unsaponifiable matter.
[2] *Zeits. f. Unters. d. Nahrgs.- u. Genussm.*, 1909, xvii. 92.

adulteration of butter by imprisonment.[1] The supervision in Denmark has been so efficient that no adulterated butter has been exported from that country during recent years. Considerable quantities of butter ·from Sweden, Norway, and Finland having been shipped to Denmark and sold as Danish butter, an Act of the 26th March 1906 deals with the marking of imported butter, and the adoption of the official mark for butter manufactured in Denmark from pasteurised cream. The importation and sale, etc., of foreign butter bearing any mark which might be mistaken for the official one has been prohibited.

The Swedish " Margarine Law," 1905, prescribes the addition of 10 per cent of sesamé oil to margarine fats. It enacts that persons who produce butter are not allowed to manufacture margarine on the same premises.

The Norwegian " Margarine Law " of 1902 enforces the control of butter manufacture by police and Government dairy inspectors, who have access to every creamery, dairy, or factory, and have the right to take samples for examination. Similarly, the imports and exports of butter are controlled by the Customs.

The Italian " Margarine Law " of 1894 defines butter as genuine (unless there are indications to the contrary) when its *Reichert-Wollny* number is not below 26 ; if the number be 20 the butter is considered as adulterated, and when it lies between 20 and 25 as suspicious. Furthermore, butter is considered as adulterated when it indicates in the butyro-refractometer at 35° C. more than 48 scale divisions (" degrees "), or when its specific gravity is below 0·865 at 100° (water at $15° = 1$).

The Siberian butter manufacturers petitioned the Government to prevent the importation of cocoa nut oil into the butter producing areas, as it was suspected that some proportion of the large amount imported was being used for the adulteration of butter.

The difficulties that were encountered formerly in the detection of foreign fats in butter have been removed to a considerable extent by the modern methods of fat analysis. But the adulterator has kept pace with the progress of fat analysis, and has succeeded, with very great ingenuity, in preparing mixtures that can only be detected by a combination of several methods. Hence, judiciously prepared mixtures of margarine and cocoa nut oil which formerly could not be recognised by the saponification value and the percentage of insoluble fatty acids alone, are no longer admixed in considerable quantities with butter, since the application of the *Reichert-Meissl (Reichert-Wollny)* method immediately discloses the fraud. Yet such mixtures are still being used extensively in small quantities, as even the *Reichert-Meissl* test breaks down when only 10 per cent of margarine are admixed with butter. As the *Reichert* value is a measure of the amount of volatile fatty acids, the author in the first edition of this work expressed the fear that the artificial butter industry might succeed in providing means to prepare butter-substitutes having a correct *Reichert* value. This fear has been realised, for butyric acid, tributyrin, and

[1] More rigorous still is the punishment for adulterating butter in Russia.

also amyl acetate are being sold (in 40 per cent alcoholic solution) for that purpose, and even patents have been taken out,[1] for the addition of volatile fatty acids to butter fat as also to margarine.[2] Such margarine will most likely find its way into butter, as its chemical characteristics only too plainly suggest fraudulent application, for the volatile acids may not only be used to improve the taste of the fatty material, as the patentees claim, but also to mislead the analytical chemist (cp. "Margarine," Chap. XV.).

Not only does the adulterator keep pace with the progress of chemical analysis, but he even adapts himself with great ingenuity to the methods to which the analysts in the different countries resort, and in particular makes excellent use of the limitations which analysts impose upon themselves (or have imposed on them by their authorities on account of the costs of an analysis) by employing "rapid" methods.[3] To give an example, the application of the refractometric method has been of very great value in the rapid analysis of butter fats, especially for purposes of market control (see below). The adulterator has, however, been able to adapt himself also to this test, as he will always adapt himself to the analyst he has to meet. Moreover the difficulties of the analytical chemist have been enhanced lately by the employment of cocoa nut oil in the adulteration of butter. Unfortunately, the practices of the adulterator are assisted to a very considerable extent by the natural vagaries in the composition of butter fat, since its chemical composition depends to a great extent on the breed (race) of the cow, the mean temperature of the country where the butter is produced, the stabling, i.e. the climatic influence to which the cows are exposed, further, on the nature and quantity of the food supplied, the period of lactation, and the idiosyncrasy of the individual cow. Notwithstanding the enormous amount of investigations that have been carried out in different countries, we are still unable to define the variations within which genuine butter fat may fluctuate. Some investigators followed the changes in the composition of butter fat obtained from a considerable number of cows, so as to eliminate the influence of one individual cow, whereas others (Klein and Kirsten) are of the opinion that only two factors, namely, food and progress of lactation, are of importance, the other factors exercising a minor influence only, so that the examination of butter fats obtained from a limited number of animals may be considered sufficient. This, however, cannot be admitted as correct, as the influence of stabling on the nature of butter has been shown to be so pronounced that during two different seasons of the year butter fats of very different composition are obtained from one and the same herd of animals.

Owing to these variations in the composition of butter fat, it is at present not possible, by merely carrying out the usual rapid tests, to detect in every given case an admixture of 10 or even 20 per cent (when the original butter had a very high Reichert value) of foreign fats. The butter adulterator keeps therefore within the limits of such

[1] English patent 22,458, 1900 ; German patent 121,657.
[2] English patent, 15,649, 1900.   [3] Cp. Jahrbuch d. Chem., 1906 (xvi.), 404.

chemical tests as are from time to time agreed upon by analytical chemists, and hence prepares on a large scale adulterated butters which just keep near the lowest limits, so that the analyst is very frequently placed in the position of having to give a butter the "benefit of the doubt," although he may feel convinced that adulteration has taken place. In this work we are not concerned with the limitations to which the public analysts are subjected, and it will be urged that the examination of butter fat must extend beyond the "quantitative reactions." In case vegetable oils or fats have been admixed with butter in a direct manner, or in an indirect manner through added margarine, in the manufacture of which vegetable fats have been used, the phytosteryl acetate test will give an unmistakable answer. If, however, animal oils or fats are used as adulterants the uncertainty mentioned above still remains. In order to pronounce on the genuineness of a sample of butter, it is therefore not only necessary to combine several methods of examination, but also, if need be, to examine the volatile acids, as also the insoluble acids separately.

The methods applicable to the detection of adulteration will be enumerated in the order of their usefulness, and the influence which the different natural factors pointed out above have on the composition of the butter fat will be discussed under each heading.

The literature bearing on the examination of butter is an extraordinarily voluminous one, and still grows. The list of methods detailed below cannot, therefore, lay claim to completeness, although no important and really valuable method will be found missing. A large number of insignificant modifications of known methods and a host of valueless proposals have been deliberately omitted.

For further information reference must be made to special works on butter.[1]

REFRACTOMETRIC EXAMINATION

The first test that is usually applied in "rapid" analysis is the determination of the refractive index of the butter fat by means of the butyro-refractometer or the oleo-refractometer. The butyro-refractometer will be found more convenient. Thus one is enabled to decide by a glance through the instrument whether a butter is grossly adulterated or whether it need only be regarded with suspicion. Owing to the rapidity with which the observation can be carried out, its importance has been sometimes overestimated, and it should therefore be distinctly remembered that the refractometric examination can only be used as a *sorting* test, and that its indications must be supported by further tests.

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[1] Sell, *Arbeiten a. d. Kaiserl. Reichsgesundheitsamt*, 1886 ; Duclaux, *Le Lait. Étude chimique et microbiologique*, Paris, 1904 ; Girard and Brevans, *La Margarine*, Paris, 1888 ; Besana, *Sui metodi a distinguere il burro artificiale dal burro naturale*, Lodi, 1888 ; Zune, *Traité général d'analyse des beurres*, 2 vols., Paris et Bruxelles, 1892.— *Report of the Departmental Committee on Butter*, Eyre and Spottiswoode, London, 1904.

The refractive indices of pure butter fats have been given in the table, p. 805. An agreement as to which temperature should be adopted as the standard for the refractometric observation has not yet been arrived at. Some observers choose 25° C., others take 40° C. The latter seems to be the most suitable standard temperature. Others again have adopted 45° C., the temperature employed by *Jean* in the observations with the oleo-refractometer.

For the refractive indices obtained with the *Abbé-Zeiss* apparatus the reader must be referred to *Hoton's* paper.[1]

All samples which give values lying outside the limits stated in the table must be looked upon as suspicious, or at least as " abnormal," and further examination is required to establish whether a sample is pure or not.

In calculating the position of the critical line found in the butyro-refractometer at 25° C. for another temperature, a correction of 0·55 scale divisions should be made for each degree C.

The following table, compiled on this basis, gives the practical limits for pure butter fats at the corresponding temperatures :—

Temperature. ° C.					Scale Division.
25	.	.	.	.	.	52·5
26	.	.	.	.	.	51·9
27	.	.	.	.	51·4
28	.	.	.	.	50·8
29	.	.	.	.	50·3
30	.	.	.	.	49·8
31	.	.	.	.	49 2
32	.	.	.	.	48·6
33	.	.	.	.	48·1
34	.	.	.	.	47·5
35	.	.	.	.	47·0
36	.	.	.	.	46·4
37	.	.	.	.	45·9
38	.	.	.	.	45·3
39	.	.	.	.	44·8
40	.	.	.	.	44·2
41	.	.	.	.	43·7
42	.	.	.	.	43·1
43	.	.	.	.	42·6
44	.	.	.	.	42 0
45	.	.	.	.	41·5

Delaite,[2] however, has shown that numbers calculated from observations made at an arbitrary temperature are not identical with those observed directly. It is therefore necessary to make the observations at the desired temperature.

If a sample furnishes numbers lying within the values given in the table, p. 805, the conclusion must not yet be drawn that the sample is genuine. For mixtures of margarine and cocoa nut oil can easily

[1] *Ann. d. falsific.*, 1909, 8.
[2] *Bull. de l'Assoc. Belge de Chimistes*, 1894 (5), 145 ; *Analyst*, 1895, 95.

be prepared showing the refractive index of a normal butter fat. It is evident that any quantity of such mixture may be added to butter with impunity, in case the refractometric observations alone are held to give a decisive answer.

The assumption of earlier observers, and unfortunately still held by some analysts, that the refraction of butter fat stands in a direct relation to the *Reichert* value, in other words, to the proportion of glycerides of volatile fatty acids (or, to be more correct, to mixed glycerides containing lower fatty acids), has not been borne out by recent evidence (cp., *e.g.* table p. 856). It is quite true that (as in the last stages of the period of lactation [*Farnsteiner and Karsch*; [1] *Masson* [2]], or in consequence of climatic conditions [*Holm, Kvarup*, and *Petersen* [3]]) the refraction increases with the decrease of volatile acids, but the refraction increases in a much greater ratio with the increase of unsaturated fatty acids; in other words, the higher the iodine value the higher will be the refraction. This becomes evident on examining the numbers which I append in the following table, bearing in mind that butter fats yielding the same amounts of volatile acids may vary in their contents of oleic acid from 10 to 15 per cent : —

Refractive Indices of Fatty Acids and their Glycerides

Acid.		$nD.$	
	° C.	Fatty Acids.	Glycerides.
Butyric . .	20	1·39906	1·43587
Caproic .	20	1·41635	1·44265
Caprylic .	20	1·42825	1·44817
Capric . . .	40	1·42855	1·44461
Lauric .	60	1·42665	1·44039
Myristic .	60	1·43075	1·44285
Palmitic . .	80	1·42693	1·43807
Stearic . .	80	1·43003	1·43987
Oleic . . .	20	1·4620	
	40	1·4546	
	60	1·4471	

It will be gathered that the small " influence " on the refractive index caused by a somewhat higher proportion of volatile fatty acids is obliterated by the greater influence of the unsaturated fatty acids.[4] This is especially shown to be the case by butter fats obtained from cows fed on linseed cake (perhaps also cotton seed meal). Minute quantities of linseed oil pass into the milk, and consequently into the butter, as is proved by the occurrence of linolenic acid in such abnormal butter fats. Therefore, as *Lobry de Bruyn* has shown first, Dutch butters are frequently met with giving deviations of − 25 to − 30, and even − 21 to − 26, in the oleorefractometer, although they con-

[1] *Zeits. f. Unters. d. Nahrgs.- u. Genussm.*, 1898, 16.
[2] *Journ. Soc. Chem. Ind.*, 1898, 861.   [3] *Biederm. Zentralblatt*, 1901, 48.
[4] Cp. also Partheil and v. Velsen, *Arch. d. Pharm.*, 1900, 261.

tained the normal amount of volatile fatty acids and had the proper flavour of good butter.

On the other hand, refractometer figures lying outside the numbers given in the tables do not unmistakably point to adulteration, but they certainly point to an " abnormal " butter. In these cases—as exemplified by " abnormal " Dutch butters [1]—further investigation must show whether the sample under examination is an adulterated butter or not.

Observations on the refraction of butter fats obtained from cows in different districts of the United Kingdom, as also from cows set apart for the purposes of an exhaustive inquiry, so that all the influences affecting the chemical composition of butter fat might be traced, were made by the Government Laboratory.[2] The observed fluctuations in the form of average values [3] are set out in the table, p. 856 ; but it should be repeated that an over-estimation must be carefully guarded against.[4] In order to study the subject in detail the reader must consult the " Bluebook." [3]

Dimitrescu and Popescu [5] determined the refractometer readings of the insoluble fatty acids and found for 48 samples of pure butter the figures 29·0-30·4, at 40° C., while in the case of 3 other samples the reading was 31·1. These authors found for the insoluble fatty acids from cocoa nut oil, lard and beef fat the readings 15·1, 37·4, and 37·4 respectively. Although the refractive index of the insoluble fatty acids lies within narrower limits than that of the fat itself, the same strictures must apply to this determination as have been given above. *v. Raalte and Lichtenbelt,*[6] however, in an examination of 530 butters found in some cases as high a reading as 36·9 for the insoluble fatty acids, so that it appears very little more information is given by the determination of this figure.

The conclusion must be accepted that the indications of the refractometer must be supported by other methods ; in the first instance, by the determination of the *Reichert-Meissl* value. Indeed, determination of the refractive index has become now of secondary importance, for reasons stated already (and to be repeated below). But it has been placed first, as the examination by this method requires less than a minute, and has, therefore, come into far greater vogue with analysts than it deserves.

[1] Cp. Lam. *Chem. Zeit.*, 1900, 394.   [2] Thorpe, *Journ. Chem. Soc.*, 1904, 248.
[3] *Report of the Departmental Committee on Butter*, London, 1904.
[4] Therefore the two tables given pp. 844, 845 of the third edition of this work have not been reproduced here.
[5] *Ann. d. falsific.*, 1910, 149.
[6] *Zeits. f. Unters. d. Nahrgs.- u. Genussm.*, 1912, iii. 82 ; cp. also Ludwig and Haupt, *ibid.*, 1907, xii. 521 ; Dons, *ibid.*, 1907, xiii. 257, 1908, xv. 81 ; Ludwig, *ibid.*, 1907, xiv. 208 ; Breen, *ibid.*, 1908, xv. 79.

The Reichert-Meissl (Reichert-Wollny) Value

The most valuable index in the chemical examination of butter fat is furnished by the determination of the *Reichert-Meissl* or *Reichert-Wollny* value.

This value is of paramount importance, for the reason that it is not possible to prepare a mixture of any fats likely to be used as butter adulterants without adding very considerable quantities of butter fat,[1] so that the mixture may have a *Reichert-Meissl* value approaching that of normal butter fat, whereas all other " values " can be adjusted by a mixture of fats other than butter fat. Thus it is easy to prepare mixtures of cocoa nut oil and beef fat (or oleomargarine) having the same refractive index, the same amount of water-insoluble fatty acids, the same saponification value, the same specific gravity, and the same iodine value as a normal butter fat, so that if any one of the criteria mentioned were applied solely, to the exclusion of the others, it would be impossible to differentiate butter fat from a mixture of the two fats named, and consequently it would be possible to add any quantity of this mixture to genuine butter fat without the adulteration being detected. It is therefore preferable to commence the examination of a butter fat with the determination of the *Reichert-Meissl* value.

The *modus operandi* has been fully described in Vol. I. Chap. VI. I omit a very large number of " new processes " which have been proposed from time to time, most of these processes being nothing but modifications and combinations of well-known methods. As an example of a superfluous method, I may mention *Kreis's* modification of *Reichert's* process, since it met with some attention. *Kreis* [2] employs for the hydrolysis of 5 grms. of butter fat 10 c.c. of concentrated sulphuric acid. The experience of several chemists, including the author, has proved that invariably sulphurous acid is liberated, which, of course, must vitiate the results unless the sulphurous acid is removed or otherwise rendered innocuous. The ingenuity of several analysts has been exercised to eliminate the error due to the presence of sulphurous acid ; others again have tried to exactly define the strength of the sulphuric acid required so as to avoid formation of sulphurous acid.

In order to prevent the possibility of the formation of ethylic esters in the saponification process, *Leffmann and Beam* proposed to saponify by means of caustic soda and glycerin. (It has been shown (Vol. I. Chap. II.) that, provided a sufficient amount of alkali be used, no ethylic esters remain unhydrolysed). This process has been adopted by several laboratories affiliated to dairies and by the German Imperial

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[1] Cp. footnote, p. 802.

[2] *Chem. Zeit.*, 1892, 1394. The statement made by Bunte (*Chem. Zeit.*, 1894, 204) that butter fat is completely hydrolysed by sulphuric acid of specific gravity 1·8355 (corresponding to 93·5 per cent of SO_4H_2) cannot be correct. On repeating Bunte's experiments Thieme (*Proc. K. Akad. Wetensch.*, Amsterdam, 1908, 855-860) obtained with sulphuric acid of 93·5 per cent, 98·5 per cent, and 100 per cent SO_4H_2 respectively, products containing in the same order 81·0 per cent, 89·7 per cent, and 92·2 per cent of free fatty acids.

" Gesundheitsamt," especially for *Polenske's* method of determining
the insoluble volatile acids. It offers many advantages as regards
rapidity of work.

From the analyses of many thousands of samples of butter fat the
fact has been deduced that the *Reichert* value is by no means so con-
stant as *Reichert's* researches have led us to believe ; the quantity of
volatile acids being influenced to a notable extent by the seasons, the
nature of the food, the period of lactation, the idiosyncrasy of the cow,
the method employed in melting the butter, its state of freshness
(rancidity), etc.

In the following table I have collated the *Reichert-Meissl* (*Reichert
Wollny*) values published by a number of observers, the *Reichert* values
(for 2·5 grms.) having been multiplied by 2·2 so as to admit of a com-
parison with the *Reichert-Meissl* (*Reichert-Wollny*) values, although
this procedure is, strictly speaking, not correct. But as the variations
in the numbers of different butter fats are greater than the error in-
volved by the employment of a necessarily inaccurate factor, the table
will be found sufficiently useful for practical purposes.

Reichert-Meissl (Reichert-Wollny) Values of Butter Fat

Origin.	Number of Samples.	c.c. decinormal KOH.	Observer.
English	?	31·9	Muter.
	7	27·6 – 29·2	Vieth.
	7	22·5	Thorpe.
	17	23·5	.,
	15	24 5	,,
	27	25·5	,,
	37	26·5	,,
	357 { 51	27·5	,,
	78	28·8	,,
	56	29·5	,,
	41	30 5	,,
	18	31·3	,,
	10	32·6	,,
Irish	300 { 15 / 33	24 up to 23	Brownlee.
Dutch—during September, October, November, December	3	17 – 18 9	van Rijn [1]
	3	19 – 19·9	,,
	8	20 – 20·9	,,
	28	21 – 21·9	,,
	34	22 – 22 9	,,
	64	23 – 23 9	,,
	428 { 74	24 – 24·9	,,
	56	25 – 25·9	,,
	67	26 – 26·9	,,
	43	27 – 27·9	,,
	34	28 – 28·9	,,
	9	29 – 29·9	,,
	5	30 – 33	,,
January/March 1910	4665 { 2 / 1030	20 – 22 / 30 and over	
April/June 1910	4774 { 2 / 1401	23 – 24 / 30 and over	
July/September 1910	4660 { 2 / 32	20 – 22 / 30 and over	
October/December 1910	4742 { 19 / 151	20 – 22 / 30 and over	
January/March 1913	4855 { 4 / 1501	23 – 24 / 30 and over	
April/June 1913	4996 { 2 / 1068	24 – 25 / 30 and over	
July/September 1913	1793 { 22 / 68	22 – 23 / 30 and over	
Oct. 17, 1900-Sept. 4, 1901—	632 [2]		
Minimum, in November	..	22·1	van Rijn.
Maximum, in March	.	33 4	,,
Danish (mixed)	7834		
Minimum	. .	22·4	Holm and Kvarup [3]
Maximum	.	33·3	
Swedish	22	26·9 – 29·4	Vieth.
	797	22·9 – 41·0	Nilson.

[1] On the Composition of Dutch Butter, London, 1902. Cp. also Reicher, Zeits. f. angew. Chem., 1901, 125 ; Clark, Analyst, 1901, 113 ; Report of the Departmental Committee on Butter. Eyre and Spottiswoode, London, 1904.

[2] From fifty-three factories.

[3] Forty-sixth Report of Danish Agricultural Laboratory. The minimum and maximum values of butters from single cows were 16·8 and 40·0 respectively.

Reichert-Meissl (Reichert-Wollny) Values of Butter Fat—continued

Origin.	Number of Samples.	c.c. decinormal KOH.	Observer.
Norwegian—			
Nov. 1898 to Dec. 1901—	657 [1]		
Minimum, in June	...	21·1	
,, in March	...	28·6	
Maximum, in August	...	31·2	
,, in January	...	84·9	
German	?	30·8	Reichert.
	?	27·0 – 31·5	Meissl.
	?	27·6 – 29·4	Reichardt.
	?	24 – 32·8	Sendtner.
	?,	22 – 32	Thorner.
North-West Germany—			
Dec. 1898 to Nov. 1899—			
Minima, in Oct.-Nov.	.	22·8 – 24·9	Vieth.
Maxima, in April-June	...	29·1 – 31·3	,,
Dec. 1899 to Nov. 1900—			
Minima, in Oct.-Nov.	...	22·4 – 24·6	,,
Maxima, in April-May	...	29·9 – 31·0	,,
French	?	29·26	Jean.
	28	26·1 – 30·6	Vieth.
	39	26·9 – 30·8	,,
Belgian	693	26 – 36·85	Wauters.
	26	25 – 25·84	,,
	16	24 – 24·96	,,
	9	23·08 – 23·84	,,
	11	19·8 – 23	,,
Italian	178	26·1 – 31·4	Corbetta.
	?	20·63	Spallanzani.
	?	19·8	Spallanzani and Pizzi.
	?	20·68	Vigna.
Minima	?	21·56	Maissen and Rossi.
	?	21·80	Besana.
	?	22·55	Longi.
	?	23·59	Sartori
Maximum	?	30·14	Spallanzani and Pizzi.
Russian—			
Minimum, in July	...	25·7	Lewin.
Maximum, in February	.	30·5	,,
October-January	161	.	Russian Bacteriological Laboratory
Minimum, in November	...	21·89	,, ,,
Maximum, in January	...	27·3	,, ,,
Minimum, in April	74	20·4	St. Petersburg City Laboratory
Maximum, in February	...	30·3	,, ,,
Baltic Provinces	...	22·6 – 36·3	Böggild. [2]
Egyptian—			
Minimum	...	24·0	Lucas.
Maximum	...	26·3	,,
Indian— [3]		25·7	Menon.

[1] From fifty-three factories.   [2] *Milchzeit.*, 1909 (38), 124.
[3] Characteristics of pure and adulterated "Ghi" from India are given by Bolton and Revis, *Analyst*, 1911. 392.

Reichert-Meissl (Reichert-Wollny) Values of Butter Fat—continued

Origin.	Number of Samples.	c.c. decinormal KOH.	Observer.
Finnish—			
January to February	?	30·0–32	
March to April	?	29·3–32	
May	?	26·5–31·1	Lewkowitsch
June to July	.	25·2–30·6	and
August	. .	24·0–29·1	Laboratorium
September	...	26·4–30·4	fur Smorunder-
October	. .	25·4–30·6	sokning in
November	. .	27·5–29·9	Hango.
December	...	28·7–31·4	
Siberian—			
Minimum	.	24·6	Lewin.
Minimum, in April	150	24·0	Russian Bacteriological Laboratory
Maximum, in August	...	30·7	,, ,,
Swiss	?	28·10–31·10	Ambuhl.
American	?	27·36	Cornwall and Wallace.

From the foregoing table it will be gathered that the *Reichert-Meissl* (*Reichert-Wollny*) values of butter fats vary considerably in different countries, and with the different seasons of the year. A sudden fall in the temperature during a period of feeding cows on turnip leaves, when the leaves were to some extent frozen, caused a sudden fall in the *Reichert* values of the milk fat.[1] It appears somewhat unjust to fix a minimum limit (as this may exclude from the market butters produced at certain seasons) ; still, in order to prevent, to some extent at least, the fraud that would be practised if the *Reichert-Meissl* (*Reichert-Wollny*) value were allowed to fall below a certain number, the minimum value for a genuine butter generally adopted amongst analysts, although not officially, in this country and France is 24, in Germany 25, and in Sweden 23. With regard to the limits fixed by law in Belgium and in Italy compare pp. 814, 815. An enormous amount of evidence has been published[2] to show that under certain conditions—which will be discussed below—the *Reichert-Meissl* value of genuine butter fat may fall, and, indeed, does fall below these limits. But it has been also proved that with proper methods of dairying and with proper feeding and stabling, even under severe climatic conditions, the characteristic amount of volatile acids, as expressed by the *Reichert* number, does not vary much, and it would therefore appear unwise to reduce those adopted limits on the strength of individual, mostly exceptional, cases. Such a procedure would undoubtedly lead to greater laxity on the part of the producers of butter. It may be objected, and indeed has

[1] Siegfeld, *Zeits. f. Unters. d. Nahrgs.- u. Genussm.*, 1909 (xvii.), 179.
[2] Cp. *Report of the Departmental Committee on Butter*, Eyre and Spottiswoode, 1904.

been objected, that by fixing a low limit, such as 23, the adulterator would be in a position to regulate his admixtures to some extent so as to keep as low a limit as possible. This might perhaps be met by raising the limit, but it should be remembered that the skilled adulterator will in any case adapt himself to given conditions, and especially to the tests applied by those analysts who are likely to examine his butter. At present enormous quantities of butter are sold in this country, the fats of which give *Reichert-Meissl* values of exactly 24. Such butters are prepared, almost on a manufacturing scale, by mixing butters rich in volatile fatty acids with margarine, the ingredients being carefully analysed before the admixture takes place.[1] Nor should greater scope be given to what has been aptly termed by *Meissl* " adulteration through the cow " (for such adulteration see below), caused by bad feeding, or by not stabling the cows when the cold season sets in, or by other conditions which influence the quality of the butter. Dutch butters furnish an instance by which this point may be illustrated. It has been proved [2] that butter made in the northern provinces of Holland during October shows lower *Reichert-Meissl* values than butters produced, on the one hand, in September, and, on the other hand, during November and December. The cause of this decrease in the amount of volatile fatty acids is due to the climatic conditions obtaining during October; after the cows have been stabled in November, the amount of volatile fatty acids again increases.[3]

The mean monthly figure for the *Reichert-Meissl* value in Altona during 1911 derived from 496 analyses was highest in May, namely, 30·2, and lowest in September, namely, 25·98.

Several years ago butters imported into the United Kingdom from the North of Holland during these critical months were repeatedly declared by analysts as adulterated, on account of their low *Reichert* values and other abnormalities. It was just this fact which led to the formation of the " Dutch Control Stations." Thus the farmers who produce such butter are now able, to prove its purity by affixing the label issued by the Dutch Department of Agriculture (see p. 814). It therefore happens not infrequently that " Dutch Control Butters " with low *Reichert* values are passed as pure, whilst without their labels they would be considered as suspicious and would even be condemned, unless convincing proof as to purity were brought by the vendor.

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[1] In this connection a table given by Wauters and Vandam in a paper, *Sur des cas de falsifications de beurres hollandais importés en Belgique*, will be found instructive. This table shows that butters obtained in Belgium through importing houses exhibit a much more uniform composition, and regularly much lower Reichert values, than butters taken from farms. Their table further shows how carefully the Reichert values are adjusted at the time of official sampling, so that at this time there are hardly any " abnormal " butters in the market.

[2] Van Rijn ; Reicher.

[3] The above observation loses in force by the fact that in Mecklenburg the lowest *Reichert-Meissl* values are obtained in the summer months when the cows are out on grass (Vieth, *Chem. Zeit.*, 1907, 1231). Hence a more likely reason for the rise of the *Reichert-Meissl* values in Holland after stalling would in Vieth's opinion appear to be caused by the change in food. But Vieth to some extent contradicts himself by pointing out that his conclusion cannot be taken as applying generally. Cp. also *Paraschtschuk* with regard to Russian butters (*Milchw. Zentralbl.* 3, 534).

It cannot be maintained that there exists any connection between the quality of butter and its chemical composition, and a butter need not be of inferior quality because it only contains a low percentage of volatile fatty acids. But even if this point be left an open question, it cannot be denied that to fix the limits too low, or to fix no limit, would be to take out of the hands of the analyst his best weapon against the adulterator and the careless farmer. Since butter from the southern provinces of Holland, where the cows are stabled at nights almost throughout the year, shows no such falling off in the amount of volatile fatty acids, it would follow that the butter manufacturer has it in his power to keep up to a standard which, for want of better analytical methods, may legitimately be considered a just and equitable one.

Similar conditions to those described above obtain in North-West Germany (*Vieth* [1]) and in Siberia ; [2] in fact they can be shown to occur in any country ; therefore butter falling below the limit of 24 (*Reichert-Wollny* number) should be considered " abnormal " if further investigation proves that no adulteration with foreign fats has taken place.

The nature of the **food** greatly influences the amount of volatile fatty acids. *Spallanzani and Pizzi* [3] have shown that when cows are out on grass the butter is rich in volatile acids, which diminish when the cows are stall fed on a *poor* ration.

This agrees with *Swaving's* experience that in the beginning of the grazing season the volatile acids increase, and remain at a high figure until the close of the season.

If cows are fed on oil cakes, the *Reichert-Meissl* value of the fat decreases considerably, in consequence of the oil passing into the milk fat. Thus it has been shown that cows fed with cotton seed cake yield butter fats of higher melting point (cp. table p. 806), with a corresponding decrease of about 1 per cent of volatile fatty acids. (It has been mentioned already that butter fat from cows fed with linseed cake behaves abnormally in the refractometric examination. [4]) *Baumert and Falke* [5] especially have shown that on feeding cows with oil cake, butter fats are obtained which exhibit *Reichert-Meissl* values corresponding to an artificial mixture of butter fat with the oils contained in the cakes. [6] Butters of this kind should at least be looked upon as " abnormal " butters, if not as inferior in quality.

Numerous experiments by other observers have proved that by selecting the food it is possible to alter the composition of the butter fat. Thus cases have occurred in which farmers who fed their cows excessively with cotton cake obtained a butter which would have been condemned, and indeed was condemned at first, as a butter adulterated

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[1] *Milchzeit.*, 1901, No. 12.

[2] Cp. *Report of the Departmental Committee on Butter*, Eyre and Spottiswoode, 1904.

[3] *Staz. Sper. Agrar. Ital.*, 38, 257.

[4] Cp. Lindsay, *Massachusetts Stat. Rep.*, 1900, 14.

[5] Cp. also A. Rufin, *Ann. de chim. anal.*, 1899, iv. 383.

[6] Cp. also A. Burr, *Milchzeit.*, 1907 (36), 289 ; 301. Knieriem and Buschmann ; v. Knorre and Girgensohn, *Chem. Zentralbl.*, 1907, ii. 835.

with about 30 per cent of oleomargarine. A manufacturer who carries out such admixture by means of dead machinery in a works would certainly be termed an adulterator; and the question may well be raised whether such adulteration "through the cow" may not be made at some future time a punishable offence; just as at present it is not permissible artificially to increase the quantity of milk by giving the cows an excess of salt.

Feeding experiments made with a view to ascertaining the cause of the deficient quantity of volatile soluble acids of the butters in the North of Holland were instituted by *Swaving*.[1] *Van der Zande*, as also *Siegfeld*, have shown that feeding with turnips increases the amount of volatile acids (water-soluble as well as water-insoluble). More recently *Siegfeld*[2] and *Amberger*[3] proved that in this case the insoluble volatile fatty acids increase at a much greater ratio than do the soluble volatile acids (*Reichert-Meissl* value). Since, at the same time, the saponification values rise considerably and the mean molecular weights of the insoluble fatty acids fall in the same ratio, whereas the iodine values become very low, a superficial consideration of the analytical figures might lead to the conclusion that adulteration with cocoa nut oil has taken place, were it not for the very high *Reichert-Meissl* values these butters showed, namely, from 31·3 to 32·9. Later *Siegfeld*[4] found the *Reichert-Meissl* to rise after feeding with turnip leaves to 35 and even to 40, and to fall at the end of the period of such feeding to 24·5. (With regard to the corresponding values for the insoluble volatile fatty acids see p. 841.) The abnormal production of volatile fatty acids seems to be due to the sugar in the turnips, for *Hoppe-Seyler* showed, many years ago, that sugar is capable of yielding by purely chemical reactions volatile fatty acids, butyric acid, caprylic acid, etc. Of great importance is the observation made by *Amberger* that food rich in proteins, such as malt germs, produces the opposite effect, in that the *Reichert-Meissl* values, titration numbers of the insoluble volatile acids, and saponification values fell considerably (in a given case, from 25·5, 1·8, and 225·5, respectively, to 16·7, 1·6, and 219·5), whilst the iodine values rose (from 32·1 to 39·2). Such butter would have been looked upon as adulterated with margarine. The experiments of *Amberger* are all the more convincing, as the feeding experiments, with turnips on the one hand, and with malt germs on the other, were carried out with one and the same set of cows. It is thus possible to produce at will a butter having the characteristics of a butter adulterated with cocoa nut oil or of a butter adulterated with margarine.

Feeding with sesamé cakes increases the yield of milk, but gives a softer butter. Arachis cakes have a marked influence on the taste of the butter. It must be borne in mind that feeding with oil cakes tends to lower the *Reichert-Meissl* value (cp. p. 827), and this fact

[1] *Zeits. f. Unters. d. Nahrgs.- u. Genussm.*, 1906, ix. 505.

[2] *Ibid.*, 1907, xiii. 516; 1909, xvii. 177.

[3] *Ibid.*, 1907, xiii. 616; 1909, xvii. 38. *Ibid.*, 1909, i. 1181. Paal and Amberger, cp. also Lührig and Hepner, *Pharm. Zentralbl.*, 1907 (48). Fritzsche, *Zeits. f. Unters. d. Nahrgs.- u. Genussm.*, 1909, xvii. 535, 1049, 1067.

[4] *Zeits. f. Unters. d. Nahrgs.· u. Genussm.*, 1909, xvii. 179.

may press hardly on the butter manufacturer, as the public analyst to whom the butters are submitted can of course have no knowledge as to how the cows have been fed.

The influence of feeding with cocoa nut cake has become of special importance, for cocoa nut oil passes into the milk fat and alters the chemical composition of the latter. Butters so obtained show high saponification values and low *Reichert-Meissl* values, such as are found in butters adulterated with cocoa nut oil (see below). The use of cocoa nut oil cakes as a food increases the yield of milk.

Great fluctuations in the composition of butter fat are caused by the **period of lactation**. *Nilson* has shown in the case of Swedish butter that the *Reichert-Meissl* value decreases from 33·44 in the first month to 25·42 in the fourteenth month of lactation. According to *Vieth*,[1] Holstein butter, made at a time when most of the cows were nearing the end of the period of lactation, gave numbers as low as 21·7 ; also *Spallanzani and Pizzi*,[2] and a number of other observers,[3] find higher *Reichert-Meissl* values in the early stages of lactation than in the later ones (*Smetham* [4]). [*Swaving*,[5] indeed, went so far as to consider on this account 14 as the permissible minimum.[6]] Similar depressions occur during the rut-time and illness of cows.

As examples of the **idiosyncrasy** of cows may be mentioned experiments carried out by *Einecke*,[7] the object of which was to demonstrate the influence of rape oil, cocoa nut oil, and linseed oil given with the food. Different individuals behaved differently to each kind of oil, and it may be mentioned that, whereas it is accepted that cocoa nut cake stimulates the production of milk and milk fat, *Einecke* found that the influence of cocoa nut oil was rather depressing than stimulating as regards the quantity of fat (see p. 633).

An especially striking example of the idiosyncrasy of cows has been described by *Fischer*.[8] Some butters were suspected on account of their *Reichert* values lying between 16·8 and 19·3. The samples taken in the stable proved that the cows did produce butter fats of such low *Reichert* values as 15·4 and 17·6. Since the food consisted largely of oil cakes (arachis cake, linseed cake, and cotton seed cake), the milk fat of the cows was examined after they had been out on grass for eight days, fourteen days, and five weeks, and the following *Reichert-Meissl* values were found respectively : 17·6, 23·6, and 22·2.

Under the heading of idiosyncrasy may also be considered the influence of the age of the animal on the composition of its milk fat.

The preservatives used may also have an influence on the *Reichert-*

[1] *Milchzeit.*, 1899, 785.

[2] *Ibid.*, 1889 461, 483.

[3] Cp., *e.g.* Paal and Amberger, *Zeits. f. Unters. d. Nahrgs.- u. Genussm.*, 1909, xvii. 44.

[4] *Analyst*, 1909, 304.

[5] *Landw. Versuchsst.*, 1891, 127.

[6] Cp. also Swaving, *Zeits. f. Unters. d. Nahrgs.- u. Genussm.*, 1905, x. 81 ; 1906, xi. 505.

[7] *Mitt. d. landw. Inst. d. Univ. Breslau*, 1903, 2, 559.

[8] *Zeits. f. Unters. d. Nahrgs.- u. Genussm.*, 1905, x. 338.

Meissl value of the fat. *Grimaldi*[1] has shown that the addition of benzoic acid to butter fat, oleomargarine, and cocoa nut oil raises the *Reichert-Meissl* values to an extent proportionate to the amount used.

Excellent as *Reichert's* method is, sophistication with 20 per cent of a foreign fat in the case of butters rich in volatile acids, or of 10 per cent in the case of butters of ordinary quality, cannot be detected with certainty in every case by the usual rapid methods. Still, *Reichert's* process must be considered the best method hitherto designed for the detection of frauds, or of "abnormal" butters, no other method allowing rapid discrimination between genuine butter and a butter adulterated with a judiciously prepared mixture of margarine and cocoa nut oil. The following table demonstrates this clearly :—

Reichert-Meissl Values

Kind of Fat	c.c. decinormal Potash.	Observer.
Cocoa nut oil	7·0-7·8	Reichert, Moore, Allen, Muter
Margarine	2·6	Muter
Oleomargarine	0·8-0·9	Jean
Butter fat with 10 per cent of cocoa nut oil .	26·8	,,
,, ,, 20 ,, ,, ,, .	24·13	,,
,, ,, 25 ,, ,, ,, .	24	Muter
,, ,, 50 ,, ,, ,, .	18	,,
,, ,, 75 ,, ,, ,, .	12	,,
50 parts of butter fat, 22·5 parts of cocoa nut oil, and 27·5 parts of oleomargarine . .	17·4	Moore

The glycerides of the volatile acids, notably acetin, have been used as butter adulterants, as it is easy to prepare a mixture of margarine and acetin having a normal *Reichert-Wollny* value. Inasmuch as acetin is soluble in water its detection becomes an easy matter.[2]

Only in those cases where margarine free from cocoa nut-oil has been used for adulteration, and its proportion exceeds 10 per cent, will the determination of the saponification value prove equally expeditious, since butter fat containing more than 10 per cent of margarine gives a low saponification value (see below). In doubtful cases it is therefore advisable to determine the saponification value as well as the *Reichert* value. Thus, in case butyric acid, butyrin, or amyl acetate have been added to conceal an admixture of margarine, an abnormally high saponification value in conjunction with a normal *Reichert* value will lead to their rapid detection. Furthermore, whenever an abnormally high saponification value is associated with an abnormally low *Reichert* value, the presence of cocoa nut oil may be suspected. In the latter event certainty is obtained by applying the phytosteryl acetate test.

[1] *Ann. Lab. Chim. d. Gabelle.*, 1912, vi. 631.
[2] Tarugi and Vernengo, *Chem. Zeit.*, 1911, 1068.

The following table presents several examples of those cases where the *Reichert-Meissl* value just reaches the figure 24, and the analyst is therefore confronted with uncertainty as to whether the butter is adulterated or not :—

No.	Fat.	Reichert Meissl Value	Oleo-refracto meter. Deviation.	Observer.
1	Genuine butter	26·29	− 30	Jean
		31·9	· 31	Muter [1]
2	Cocoa nut oil	7·8	− 59	Jean
	,, ,, ...	7 7	− 51	Muter
3	Genuine butter with 10 per cent of cocoa nut oil	26 8	− 33	Jean
4	,, ,, 15 , ··		− 31	,,
5	,, , 20 ,, ,.	24·13	− 36	,,
6	,, ,, 25 ,, ·,	26·4	− 39	Muter
7	,, ,, 50 ,, ,,	19 8	− 14	,,
8	,, ,, 75 ,, ,,	13 2	− 49	,,
9	Margarine	2 8	− 8·5	,,
10	Genuine butter with 25 per cent of margarine	24	− 27	,,
11	,, ,, 50 ,, ,,	17·1	− 22	,,
12	,, ,, 75 ,, ,,	9 9	− 15	,,
13	Margarine with 50 per cent of cocoa nut oil .	6·1	− 52	,,
14	50 per cent genuine butter with 25 per cent of margarine and 25 per cent of cocoa nut oil	19·3	· 33	,,
15	25 per cent genuine butter with 50 per cent of margarine and 25 per cent of cocoa nut oil	12·3	− 27	,,

The specimens represented by Nos. 3 and 4 of the foregoing table cannot be reported as adulterated samples if judged by the *Reichert-Meissl* value and by the refractometric method alone.

The adulterator has taken advantage of this fact, and hence—especially in Belgium—large amounts of butter were undoubtedly adulterated with cocoa nut oil.

In cases of this kind, the **phytosteryl acetate test** leads unmistakably to the detection of vegetable oils. *Hanus and Petrik* [2] state that by the examination of the ethylesters 10 per cent of cocoa nut oil can be determined in butter. For the details of their method the original paper should be consulted.

Since this test demands a considerable amount of time, as well as of material, it has been attempted to detect cocoa nut oil in butter fat by a more rapid method, aiming at the determination of the water-insoluble volatile acids.

[1] The Reichert values given by *Muter* have been multiplied by 2·2 for the sake of better comparison.

[2] *Chem. Zeit.*, 1910, 736.

The Water-insoluble Volatile Fatty Acids

Titration Number of Insoluble Volatile Fatty Acids

The principle underlying the detection of cocoa nut oil by this method rests on the fact that by far the greater part of the volatile fatty acids of *butter fat* obtained in *Reichert's* distillation process is soluble in water, a small quantity only being insoluble, whereas in the case of *cocoa nut oil*, a small amount only of the volatile acids obtained by the *Reichert* distillation process is soluble in water, by far the larger amount being insoluble. By titrating separately these two kinds of fatty acids with decinormal potash, a great difference between butter fat on the one hand and cocoa nut oil on the other will be observed. This difference can also be traced in butters adulterated with comparatively small quantities of cocoa nut oil (about 10 per cent). This principle was proposed by *Salkowski*[1] and later on has been made use of by *Hart*,[2] *Wauters*,[3] *Vandam*,[4] and *Reychler*.[5] *Wauters* required (on applying his method of distilling twice) 11·4 c.c. of decinormal potash for the soluble volatile acids of cocoa nut oil and 15·4 c.c. for its insoluble volatile acids, whereas several samples of butter fat (taking the mean of three samples) required 27·9 c.c. for the soluble volatile acids and 0·9 c.c. for the insoluble volatile acids.

Although the details of *Wauter's* process have been criticised by *Ranwez*,[6] the underlying principle is a sound one (cp. also *Jean*[7]). It has been carefully worked out almost simultaneously by *Müntz and Coudon*[8] in France, and by *Polenske*[9] in Germany, to a new method for determining cocoa nut oil in butter.

In order to obtain constant and comparable results it is necessary that the minutest details be observed in carrying out the determinations, and it must further be considered as an indispensable condition that the apparatus should conform in every respect to that described by the respective authors.

Müntz and Coudon weigh out accurately, with the aid of a finely drawn-out tube, 10 grms. of filtered butter fat, melted to a clear liquid, into a cylinder of 5 cm. diameter and 8 cm. height, provided with a spout, and tared on an accurate balance. Before the butter commences to solidify, 5 c.c. of a hot concentrated solution of caustic potash are added. The potash solution is prepared by dissolving 120 grms. of caustic potash (pure from alcohol), with exclusion of air, in hot water, which is added in small quantities, so that the final volume of the

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[1] *Zeits. analyt. Chem.*, 1887, xxvi. 582.   [2] *Chem. Zeit.*, 1901, 207.

[3] *Bull. de l'Assoc. Belge. de Chim.*, 1901, 258.   Cp. *Bull. du Service de Surveillance*, etc., 1907.

[4] *Ann. de Pharm. de Louvain*, 1901, 201.   *Analyst*, 1901, 320.   For a criticism of Vandam's method, cp. Fendler (*Arbeit. a. d. Pharm. Inst. d. Univ.*, Berlin, 1908).

[5] *Bull. de la Soc. Chim.*, 1901, 142.

[6] *Ann. Pharm.*, 1901, 241.   Cp. Van Leent, *Chem. Centralbl.*, 1903, ii. 1193.

[7] *Ann. Chim. Anal. Appl.*, 1903, 441.

[8] *Annales de l'Institut national agronomique*, 1904, [3] (2), Fasc. 1.

[9] *Arbeit. a. d. Kaiserl. Gesundheitsamte*, 1904, 545.

solution, whilst still warm, does not exceed 100 c.c. Should this solution crystallise on cooling, it should be heated on a water-bath until it becomes clear, when small quantities of water are added so that the solution may remain clear at a temperature of 20° C.

With the aid of a glass rod, flattened at the end, the caustic potash is intimately mixed with the butter fat, and the mixing is continued for at least twenty minutes, so as to bring the butter fat particles into intimate contact with the potash. The mass becomes hot at first; when it has become hard, the cylinder is placed in an oven heated to
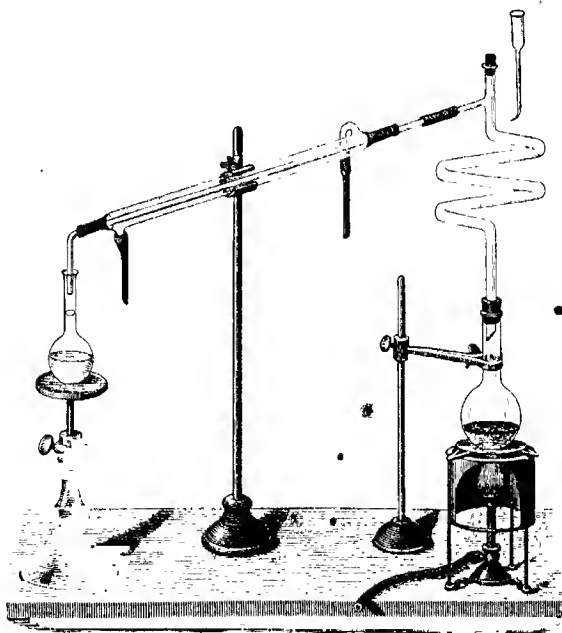
FIG. 15.

70-80° C., and left therein for twenty minutes; this is sufficient to effect complete saponification. With the aid of the glass rod the hard soap is broken up and reduced to a coarse powder. This is then transferred with the aid of 200 c.c. of distilled water, accurately measured off, into a distilling flask. The flask is gently heated over a Bunsen burner with frequent shaking, care being taken that no loss of water occurs through evaporation. When the soap is dissolved completely and cooled down to the ordinary temperature, 30 c.c. of a phosphoric acid solution of 1·15 specific gravity are added. (This solution is prepared by dissolving syrupy phosphoric acid of 45° Bé in about twice its volume of water.) Finally, a few pieces of pumice stone are introduced.

The carbonic acid which is combined with the potash would render

the determination incorrect ; in order to remove it the flask is con-
nected with a vacuum pump and exhausted for ten to fifteen minutes,
while the cold, acid solution is carefully shaken. The distilling flask
is fitted with a dephlegmator, and is connected with a condenser exactly
as shown in the figure. The distilling flask is of Bohemian glass, and
holds 500 c.c. up to the commencement of the neck ; the latter is 9
cm. long and has a diameter of 20 mm. The dephlegmator is made
from a glass tube 1 meter long, having an outside diameter of 16 mm.
and inside diameter of 14 mm. It is bent exactly as is shown in the
illustration. The lower end is cut off aslant ; a side tube is sealed into
the upper end. The upper end of the dephlegmator is closed by an
india-rubber stopper. The dephlegmator has a vertical height of 35
cm. ; about 92 cm. of the total length of the tube thus serve for cooling
the vapours.

The flask is heated direct over a Bunsen burner ; in order to avoid
overheating of the sides, especially towards the end of the distillation,
the flask is placed on a copper ring of 13 cm. diameter, having a hole
6 cm. in diameter. The flame is so regulated that the distillation lasts
about one hour and a half. The distillate is received in a 200 c.c.
graduated flask. The distillation is interrupted when exactly 200 c.c.
have distilled over.

The liquid in the measured flask is more or less turbid, and on its
surface there float oily drops of insoluble volatile acids. In order
to facilitate the separation of the insoluble volatile acids from the
soluble volatile acids, the liquid is allowed to stand till the following
day, and is then filtered through a moistened filter paper. The in-
soluble acids remain on the filter, and the soluble acids are collected
in a 750 c.c. beaker. The flask is washed with 5 c.c. of water, which
are also thrown on the filter.

All these precautions are indispensable in order to obtain a good
separation of the soluble from the insoluble volatile acids, as other-
wise, e.g. if the time allowed for separation were shortened, small
quantities of insoluble acids would pass through the filter, which would
be indicated by the turbid appearance of the filtered liquid. In order
to obtain constant results it is indispensable that the aqueous solution
should be perfectly clear. To the clear filtrate six drops of a 1 per
cent solution of phenolphthalein are added and the liquid titrated
with standardised lime water. 100 c.c. of the lime water are run in
at once from a pipette, and the titration is then completed with the
same standard lime solution added from a burette. The titration is
finished when the pink colour persists in the liquid for a few seconds.
The number of c.c. of lime solution used for titration is calculated to
butyric acid.

The insoluble volatile acids which have remained to the largest
extent on the filter, and traces of which still adhere to the 200 c.c.
flask, as also to the cooling tube of the condenser, are collected by
placing the filter on the 200 c.c. flask and treating it with four suc-
cessive washes of alcohol of 5 c.c. each, allowing the alcohol to fall
drop by drop from a pipette on to the filter. The 200 c.c. flask is then·

placed under the condenser, the outlet of which has meanwhile been closed by means of an india-rubber tube and pinch-cock. The condenser is detached from the dephlegmator, and about 200 c.c. of alcohol are run into the cooling tube of the condenser through a small funnel. The alcohol is allowed to remain for some minutes in the tube and is then run into the 200 c.c. flask by opening the pinch-cock. The condenser tube is washed once more with 5-6 c.c. of alcohol. The alcohol must be neutral, and be of 95 per cent (*Gay Lussac* ?). The insoluble volatile acids, which are now completely collected in the 200 c.c. flask, are titrated (after addition of four drops of phenolphthalein solution) with standard lime solution, which is allowed to run in from a burette. The quantity of volatile insoluble acids is also expressed in terms of butyric acid.

It will be seen that *Müntz and Coudon* deviate from the *French official method* (described Vol. I. Chap. VIII.) in the determination of the volatile acids, and approach the method of *Reichert-Meissl* with this important difference that they employ double the quantity of material and collect twice the volume of distillate. I append, in the following table, the results obtained by *Müntz and Coudon* in the examination of forty butters obtained from different departments of France :—

No.	Soluble Volatile Acids.	Insoluble Volatile Acids.	Relation (Rapport).
	In Terms of Butyric Acid.		$\dfrac{\text{Insol. Vol. Acids}}{\text{Sol. Vol. Acids}} \times 100.$
	Per cent.	Per cent.	
1	5·55	0·57	10·3
2	6·01	0·77	12·8
3	6·00	0·75	12·5
4	5·10	0·50	9·9
5	5·14	0·73	14·2
6	5·52	0·63	11·4
7	5·62	0·69	12·3
8	5·72	0·52	9·1
9	5·50	0·65	11·8
10	5·38	0·50	9·2
11	5·24	0·50	11·4
12	5·94	0·63	10·5
13	5·73	0·66	11·6
14	5·54	0·79	14·3
15	5·70	0·87	15·1
16	5·86	0·61	10·5
17	5·52	0·61	11·0
18	5·61	0·79	14·2
19	5·44	0·75	13·7
20	5·55	0·68	12·2
21	5·24	0·71	13·5
22	5·70	0·69	12·1
23	5·19	0·59	11·3
24	4·83	0·67	13·8
25	4·79	0·68	14·1
26	5·61	0·60	10·7
27	5·47	0·72	13·2
28	5·24	0·55	10·5
29	5·45	0·64	11·8
30	5·19	0·81	15·6
31	5·02	0·59	11·7
32	5·47	0·54	9·8
33	5·07	0·58	11·4
34	5·26	0·68	12·9
35	5·14	0·71	13·8
36	5·18	0·69	13·3
37	5·01	0·59	11·8
38	5·01	0·64	12·7
39	5·43	0·51	9·3
40	5·20	0·54	10·3
		Average 0·652	12·04
		Minimum 0·50	9·1
		Maximum 0·87	15·6

On referring to p. 642 it will be gathered that the relation :—
insoluble volatile acids ÷ soluble volatile acids × 100 varies for cocoa
nut oil between the numbers 250·3 and 314·7. The enormous differ-
ence which exists in this respect between butter fat and cocoa nut oil
permits the recognition of an admixture of cocoa nut oil to butter.
This is confirmed by the following table, in which I have collated a
number of figures published by *Müntz and Coudon* :—

	Soluble Volatile Acids.	Insoluble Volatile Acids.	Relation.
	In Terms of Butyric Acid.		$\dfrac{\text{Insol. Vol. Acids}}{\text{Sol. Vol. Acids}} \times 100.$
	Per cent.	Per cent.	
Mixtures of Pure Butter with 20 per cent Cocoa Nut Oil, No. 1 (p. 642)			
1. Pure butter (Sarthe) . .	5·67	0·71	12·5
Do. · containing 20 per cent cocoa nut oil . .	4·82	1·31	27·2
2. Pure butter (Normandy) . .	5·88	0·62	10·6
Do. containing 20 per cent cocoa nut oil . .	5·09	1·28	25·0
3. Pure butter (Bretagne) . .	5·56	0·56	10·0
Do. containing 20 per cent cocoa nut oil . .	4·81	1·40	29·0
Mixtures of Pure Butter with 15 per cent Cocoa Nut Oil, No. 1 (p. 642)			
1. Pure butter (Seine Inférieure) .	5·34	0·69	12·9
Do. containing 15 per cent cocoa nut oil . .	4·71	1·19	25·2
2. Pure butter (Sarthe) . . .	5·67	0·71	12·5
Do. containing 15 per cent cocoa nut oil . .	5·03	1·10	21·9
3. Pure butter (Finistère) . .	5·52	0·63	11·4
Do. containing 15 per cent cocoa nut oil . .	4·71 ·	1·11	23·6
Mixtures of Pure Butter with 12·5 per cent Cocoa Nut Oil, No. 1 (p. 642)			
1. Pure butter (Vendée) . . .	5·71	0·73	12 8
Do. containing 12·5 per cent cocoa nut oil .	5·20	1·16	22·4
2 Pure butter (Charente-Inférieure)	5·24	0·71	13·5
Do. containing 12·5 per cent cocoa nut oil .	5·19	1·08	20·7
3 Pure butter (Charente-Inférieure)	5·44	0·75	13·7
Do. containing 12·5 per cent cocoa nut oil .	4·84	1·23	25·3

Mixtures of Pure Butter with 10 *per cent Cocoa Nut Oil, No.* 2 (p. 642)

	Soluble Volatile Acids.	Insoluble Volatile Acids.	Relation.
	In Terms of Butyric Acid.		$\frac{\text{Insol. Vol. Acids}}{\text{Sol. Vol. Acids}} \times 100.$
	Per cent.	Per cent.	
1. Pure butter (Seine Inférieure) .	5·34	0·69	12·9
Do. containing 10 per cent cocoa nut oil .	4·90	1·01	20·6
2. Pure butter (Morbihan) .	5·56	0·56	10·0
Do. containing 10 per cent cocoa nut oil .	5·23	1·03	19·6
3. Pure butter (Vendée). .	5·73	0·66	11·6
Do. containing 10 per cent cocoa nut oil .	5·30	1·02	19·2

Exactly the same principle underlies the method of *Polenske*, who works with 5 grms. of butter fat, and adapts himself more completely to the *Reichert-Meissl* (*Wollny*) method than *Müntz and Coudon* did.

Polenske [1] ascertained, by examining thirty-four samples of butter fat, the *Reichert-Meissl* values of which varied from 23·3 to 30·1, that the amount of decinormal alkali required for the insoluble volatile fatty acids varied from 1·5 to 3·0 c.c., whereas in the case of four samples of cocoa nut oil having the *Reichert-Meissl* values 6·8 to 7·7, as much as 16·8 to 17·8 c.c. of decinormal potash were required for the neutralisation of the insoluble volatile acids. (The number of c.c. of decinormal alkali required for the neutralisation of the *insoluble* volatile fatty acids was termed by *Polenske* " new butter value.")   *Polenske* further lays stress on the fact that the insoluble volatile fatty acids of butter fat form oily drops, if the *Reichert-Meissl* value of the butter fat be low, or a semi-solid, non-transparent mass in case the *Reichert-Meissl* value be high.   He further observed that if 10 or more per cent of cocoa nut oil be admixed to butter fat, the insoluble volatile acids no longer solidify.   (This is explained by *Polenske* by the fact that the volatile acids of cocoa nut oil contain large quantities of caprylic acid, whereas in the case of butter fat capric acid predominates.)

A large number of experiments have demonstrated that it is absolutely necessary to follow the process in all its minutest details, in order to obtain concordant results.

If the *Leffmann-Beam* method for saponification is adopted, care must be taken to use exactly 20 grms. of glycerin for each test, since *Arnold* [2]

[1] Cp. Vol. I. p. 425.
[2] *Zeits. f. Unters. d. Nahrgs. u. Genussm.*, 1912, viii. 391.

states that the amount of insoluble volatile acids varies directly with the amount of glycerin. This is, no doubt, due to the higher boiling point of the acid liquid. *Arnold* also advises, in order to guide the operator, the use of lard in a blank test, the *Polenske* value of which should be about 0·5.

In the following table I reproduce a number of values published by *Polenske* for pure butter fats, and for the same butter fats after they have been admixed with 10 per cent, 15 per cent, and 20 per cent of cocoa nut oil respectively :—

	Number of c.c. $\frac{1}{10}$ norm. KOH, "Titration Numbers," required for the Neutralisation of the							
No	Soluble Volatile Acids (R.-M. Value).	Insoluble Volatile Acids	Soluble Volatile Acids (R.-M. Value).	Insoluble Volatile Acids	Soluble Volatile Acids (R.-M. Value).	Insoluble Volatile Acids.	Soluble Volatile Acids (R.-M. Value).	Insoluble Volatile Acids.
	of Pure Butter Fat.		of Same Butter Fat containing 10 per cent of Cocoa Nut Oil.		of Same Butter Fat containing 15 per cent of Cocoa Nut Oil.		of Same Butter Fat containing 20 per cent of Cocoa Nut Oil.	
1	19·9	1·35	18·7	2·4	18·1	2·9	17·6	3·3
2	21·1	1·4	19·7	2·3	19·2	3·0	18·5	3·6
3	22·5	1·5	21·0	2·5	20·4	2·9	19·8	3·5
4	23·3	1·6	22·0	2·5	21·5	3·1	21·0	3·7
5	23·4	1·5	22·3	2·1	21·7	3·1	21·2	3·7
6	23·6	1·7	22·5	2·5	21·9	3·3	21·4	4·0
7	21·5	1·6	23·3	2·5	22·4	3·1	21·7	3·7
8	24·7	1·7	23·8	2·9	22·9	3·5	22·1	3·9
9	24·8	1·7	23·5	2·7	22·7	3·2		
10	24·8	1·6	23·4	2·5	22·8	3·0	22·1	3·6
11	25·0	1·8	23·0	2·7	23·3	3·1	21·8	3·6
12	25·1	1·6	23·5	2·5	23·1	3·0	22·5	3·8
13	25·2	1·6	23·4	2·6	22·9	3·0	22·3	3·7
14	25·3	1·8	24·0	2·9	23·5	3·5	22·6	4·1
15	25·4	1·9	24·2	3·0	23·7	3·6	22·6	4·1
16	25·6	1·7	24·1	2·7	23·3	3·1	22·7	3·7
17	25·4	1·7	23·8	2·6	23·0	3·1		
18	26·2	1·9	25·0	3·1	24·2	3·6	23·6	4·0
19	26·5	1·9	25·0	2·9	24·1	3·5	23·2	4·1
20	26·6	1·8	25·4	2·9	24·6	3·3	23·9	3·8
21	26·7	2·0	25·2	3·2	24·5	3·6	23·7	4·2
22	26·8	2·0	24·8	3·0	24·2	3·4	23·5	4·0
23	26·9	2·1	25·2	2·9	24·1	3·6	23·2	4·2
24	26·9	1·9	24·9	2·9	24·0	3·3	23·3	4·0
25	27·5	1·9	25·7	2·7	24·9	3·3	24·0	3·9
26	27·8	2·2	26·0	3·1	25·0	3·7		...
27	28·2	2·3	26·1	3·1	25·1	3·8	24·5	4·4
28	28·4	2·3	26·5	3·5	25·7	4·0	25·1	4·5
29	28·8	2·2	26·8	3·3	26·0	3·9	..	...
30	28·8	2·5	27·1	3·5	26·3	4·0	25·4	4·7
31	29·4	2·6	27·6	3·8	26·9	4·2		...
32	29·6	2·8	27·5	3·8	26·2	4·2	25·5	4·9
33	29·5	2·5	27·4	3·5	26·6	4·1	25·4	4·7
34	30·1	3·0	27·8	3·8	26·9	4·4	26·2	5·0

With the assistance of this table *Polenske* claimed to be able to

calculate quantitatively (though only approximately) the admixed cocoa nut oil in an adulterated butter fat, relying on the conclusion derived from the thirty-four given samples, viz. that the amount of alkali required for the neutralisation of the insoluble volatile acids is increased by 0·1 c.c., through the addition of 1 per cent of cocoa nut oil. An example may illustrate his manner of calculation :—A sample of butter fat gave the *Reichert-Meissl* value 24·5, and required for the neutralisation of the insoluble volatile fatty acids 3·0 c.c. of decinormal alkali. The insoluble volatile acids were found to be liquid. According to the foregoing table, a *pure* butter fat of the *Reichert-Meissl* value 24·5 requires only 1·6 c.c. of decinormal alkali for the neutralisation of the insoluble volatile acids ; hence, there was used an excess of 3·0 − 1·6 = 1·4 c.c. for the neutralisation of the insoluble volatile fatty acids. The sample must therefore be judged to have been adulterated with cocoa nut oil. Since each 0·1 c.c. is taken to correspond to 1 per cent of added cocoa nut oil, the sample would contain 14 per cent of cocoa nut oil. Examples 15 and 22 of the foregoing table (24·2 ; 3·0 and 24·8 ; 3·0) would point to an admixture of 10 per cent of cocoa nut oil. The sample which gave these numbers actually did contain 10 per cent of cocoa nut oil.

Sundberg [1] dissents from this method of calculation as he states that it gives the amount of cocoa nut oil expressed as a percentage of the butter fat present, which figure must be reduced to the percentage of the mixture. He adduces the following example as proof of his statement :—A mixture containing 20 per cent of cocoa nut oil had a *Reichert-Meissl* value of 23·7, and a *Polenske* value of 4·4. The quantity of cocoa nut oil according to *Polenske's* table would be $(4·4 − 1·7) \times 10 = 27$ per cent. Expressed in terms of the mixture, this figure would be reduced to 21·3 per cent.

A table showing the influence which the amount of fat taken exercises on the *Reichert-Meissl* value and titration number of the insoluble volatile acids is given in Vol. I. p. 536.

Although these methods must be considered as valuable additions to the armoury of the analytical chemist, the fact should not be overlooked that some uncertainty adheres to them, especially as regards the quantitative interpretation, since the value of these methods can be rendered nugatory by the employment of smaller quantities of cocoa nut oil than 10 per cent, or of a mixture of cocoa nut oil and margarine or of edible palm kernel oil instead of cocoa nut oil.

Unfortunately the results obtained by the two methods are not comparable, and it must therefore be repeated once more that it is necessary strictly to adhere to the working conditions laid down by *Müntz and Coudon* on the one hand and by *Polenske* on the other if it be desired to institute a comparison with the above given figures. Moreover, it must not be overlooked that in the examples given above the composition of both the original butter and the admixed cocoa nut oil were known. This is of course not the case if a commercial

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genüssm.*, 1913, xxvi. 422.

sample be under examination. Whereas the composition of cocoa nut oil does not fluctuate within wide limits (see, however, below), the vagaries of butter fat may, in case only small additions of cocoa nut oil have been made, entirely nullify the indications to be drawn from the above given tables.

Polenske in his original communication gave a table setting out the maximum permissible titration numbers for the insoluble volatile acids of butter fats corresponding to all *Reichert-Meissl* values lying between 20 and 30. I have not reproduced this table, as in my own experience with different butter fats examined by *Polenske's* method, I found that the assumed regularity which he had derived from his figures did not hold good for my specimens. Thus, whereas *Polenske* gave the titration numbers for the insoluble volatile acids of butter fats having *Reichert-Meissl* values from 29 to 30 as 2·5-3·0, with the maximum permissible limit of 3·5, I have obtained the following figures with a number of undoubtedly pure French and Finnish butters :—

Titration Numbers of Soluble and Insoluble Volatile Acids (Lewkowitsch)

Soluble Volatile Acids Reichert-Meissl Value.						Insoluble Volatile Acids.
29·3	.	.			.	3·29
29·31	.	.	.	.	.	3·19
29·32	.	.	.	.	.	2·53
29·37	.	.	.	.	.	2·80
29·96		.	.	.	.	2·24
30·02		.	.	.	.	3·27
30·15	.	.	.	.	.	3·24
30·49		.	.	.	.	3·50
31·0		.	.	.	.	3·06
31·41			.		.	4·1
31·49					.	3·6
31·99	.			.	.	3·03

For butters obtained from cows which have been fed on turnip leaves, *Siegfeld* [1] found the following titration numbers :—

Soluble Volatile Acids Reichert-Meissl Value.						Insoluble Volatile Acids.
35·35	.	.	.	.	.	5·00
40·30	.	.	.	.	.	6·20
30·15	.	.	.	.	.	3·30
30·45	.	.	.	.	.	3·10
33·45	.	.	.	.	.	4·40
31·60	.	.	.	.	.	4·90
29·1					.	4·05
24·45	.	.	.	.	.	2·05

It must be conceded that in the face of these numbers no fixed rule as to maximum permissible numbers, and consequently as to the presence of cocoa nut oil in the case of an unknown sample, can

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909 (xvii.), 179.

be derived from the titration numbers of the insoluble volatile acids, although *Barthel and Sonden*[1] state that a large number of Swedish butters examined by them during the years 1904 to 1912 never showed figures for the insoluble volatile acids exceeding those given by *Polenske*. It should, further, be added that the limits given by *Polenske* for the insoluble volatile acids of cocoa nut oil cannot be accepted as having general applicability, for I have found for a number of edible cocoa nut oils of the *Reichert-Meissl* values 7·32 to 7·5, titration numbers of the insoluble volatile acids lying between 15·49 and 20·45. Furthermore, it should be noted that if palm kernel oil instead of cocoa nut oil be admixed with butter fat much smaller titration numbers will be found for the insoluble volatile acids, since palm kernel oil yields, in *Polenske's* test, numbers lying between 10 and 12.

Whereas the method proposed by *Müntz and Coudon* has not been made the subject of further publications, a large number of observers have repeated *Polenske's* experiments, and have confirmed the strictures I have expressed above. Amongst those observers are *Hesse*,[2] *Wiedmann*,[3] *Arnold*,[4] *Farnsteiner*,[5] *O. Jensen*,[6] *Lührig*,[7] *Siegfeld*,[8] *Kühn*,[9] *Rideal and Harrison*,[10] *Thorp*,[11] *Kühn*,[12] *Fritzsche*,[13] *Tatlock and Thomson*,[14] and *H. T. Cranfield*.[15] *Siegfeld* has published a considerable number of analyses of genuine butters, and has shown that the generalisation expressed by *Polenske's* additional table (omitted in this work) does not hold good, that wide deviations therefrom must be allowed, and that the titration numbers of the insoluble volatile acids are subject to the same fluctuations as the *Reichert-Meissl* values. Nay, it has even been demonstrated that through the vagaries of butter fat the titration numbers of the insoluble volatile acids are liable to greater fluctuations than the *Reichert-Meissl* numbers themselves.[16] The titration numbers appear to vary much more through the influence of food than does the *Reichert-Meissl* number, especially if cocoa nut cake has been used.

Nor have more recent observations confirmed *Polenske's* statement that the insoluble volatile acids of butter fat no longer solidify in case 10 per cent or more of cocoa nut oil have been admixed with the butter. For I have frequently observed that genuine butters with high *Reichert-Meissl* values yielded insoluble volatile acids, which did not solidify at 15° C.

It must, therefore, be concluded that the results obtained in the determination of the insoluble volatile acids by either method must

[1] *Zeits. f. Unters. d. Nährgs- u. Genussm.*, 1914, xxvii. 439.
[2] *Milchw. Centralbl.*, 1905, i. 13.
[3] *Molkerei Zeit. Hildesheim*, 1904, 18, 29.
[4] *Zeits. f. Unters. d. Nährgs- u. Genussm.*, 1905, x. 202.
[5] *Ibid.*, 1905, x. 51.
[6] *Ibid.*, 1905, x. 276.   [7] *Ibid.*, 1906, xi. 14.
[8] *Milchw. Centralbl.*, 1906 (4), 289 (7), 145.
[9] *Ibid.*, 1907, xiv. 741.
[10] *Analyst*, 1906, 256.   [11] *Ibid.*, 1906, 357.
[12] *Zeits. f. Unters. d. Nährgs- u. Genussm.*, 1907, xiv. 743.
[13] *Ibid.*, 1908, xv. 193.
[14] *Journ. Soc. Chem. Ind.*, 1909, 69.
[15] *Analyst*, 1911, p. 446.
[16] *Cp. Zeits. f. Unters. d. Nährgs- u. Genussm.*, 1909 (xvii.), 37.

be looked upon with great circumspection, and that *no definite conclusions* can be drawn, unless they are supported by other evidence—chiefly the phytosteryl acetate test (see below).

It should be remembered that when cows are fed with cocoa nut cake their milk fat simulates, in its chemical composition, a butter fat to which small quantities of cocoa nut oil have been admixed, in that it exhibits a low *Reichert* value and a high saponification value, and also a high titration number of the insoluble volatile fatty acids. This pitfall should at present be especially guarded against, as in consequence of the enormous expansion of the edible cocoa nut oil industry very large quantities of cocoa nut cake are given to milch cows (see p. 633). Though butters obtained from cows so fed are genuine they may raise grave suspicions in the mind of the analyst when " abnormal " figures are obtained.

To give an example, *Juckenack and Pasternack* [1] have published the following analyses of two genuine butter fats, which were looked upon as extremely suspicious on account of the analytical data which they furnished :—

	Butter No 1.	Butter No. 2.
Saponification value	236·95	235·80
Reichert-Meissl value	27·05	27·15
Titration number of insoluble volatile acids . .	3·50	2·40
Mean Molecular Weight of the insoluble fatty acids	253·05	252·45

It should further be borne in mind that feeding with turnips, or turnip leaves, increases the titration numbers of the insoluble volatile fatty acids in a much higher degree than the titration numbers of the soluble volatile fatty acids (*Reichert-Meissl* values), so that also through this cause unjustified suspicion may be raised against butters in which the proportion of insoluble volatile to soluble volatile acids deviates considerably from the figures quoted above.[2]

In such cases it is absolutely necessary to have recourse to the phytosteryl acetate test, as this leads unmistakably to the detection of cocoa nut oil, for it has been pointed out (p. 670) that numerous experiments have demonstrated that any phytosterol given with the food does not pass into the milk fat. Therefore it is easy to distinguish butter fats to which cocoa nut oil has been added fraudulently from those butter fats which simulate adulterated specimens through the fact that the milch cows have been fed with cocoa nut cake. Since the phytosteryl acetate test reveals the smallest quantities of vegetable fat present, it is possible by this means to detect with certainty 10 per cent (and even less) of fraudulently added cocoa nut oil.

In order to prove this by actual experiments the author prepared mixtures of pure butter with 10 per cent of cocoa nut oils, containing 0·23 per cent and 0·179 per cent respectively of unsaponifiable matter. In the following table the results of this examination are tabulated :—

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[1] *Zeits. f. Unters. d. Nahrgs. u. Genussm.*, 1906, xi. 159.
[2] (Paal and Amberger), *ibid.*, 1909, ii. 237.

Phytosteryl Acetate Test with pure Butter Fat, pure Cocoa Nut Oil, and with a Mixture containing 10 per cent of Cocoa-Nut Oil (Lewkowitsch)

	Pure Butter Fat. ° C.	Pure Cocoa Nut Oil. ° C.	Mixture of pure Butter Fat with 10 per cent of Cocoa Nut Oil, yielding Unsaponifiable Matter.	
			0·23 per cent.	0·179 per cent.
Melting point of 2nd crop of crystals .	112	129-130	115-117	113·5
Do.　　5th　　do.	113·5	...	123-124	123·0
Do.　　7th　　do.	113·5	...	...	...

This is confirmed by *Kedrevitsch*,[1] who found 0·09 to 0·3 per cent of crude phytosterol yielding an acetate melting at 122 to 125° C. in cocoa nut oil, whereas butter fat contained 0·3 per cent of crude cholesterol yielding an acetate melting at 113 to 113·5° C.

It should not be forgotten that the information furnished by the phytosteryl acetate test, as carried out ordinarily, may be rendered nugatory by the fraudulent addition of a small amount of paraffin wax to the butter fat. It has been shown above (" Lard," p. 719) how the paraffin wax can be eliminated, so that the indications of the phytosteryl acetate test become absolutely reliable.

I wish to emphasise again that, if serious errors are to be avoided, in each doubtful case the indications of the insoluble volatile acid test must be supplemented by the phytosteryl acetate test.

Altogether futile must be judged the attempt of some analysts to derive the conclusion that an admixture of beef fat or lard has taken place if only low titration numbers for the insoluble volatile acids are found. This erroneous conclusion had indeed been propounded within the author's experience in the case of a number of butter fats having *Reichert-Meissl* values of about 25·6 to 26·2, and the titration numbers (for the insoluble volatile acids) 2·01 to 2·06, because the additional table published by *Polenske* (omitted here for the reasons stated above) indicated that the titration number should be 2·4.[2] It need hardly be pointed out that conclusions resting on such slavish adherence to figures derived from too small a number of observations on butters produced within a limited area are entirely devoid of general applicability. Emphasis should be laid on this, since it may happen that a miscarriage of justice may follow, especially if, on the strength of such erroneous

[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1912 (xxiv.), 334.

[2] In fact, as palmitic acid distils over under the conditions of the test in not altogether negligible quantities (cp. *e.g.* table, p. 700), the titration number of the insoluble volatile acids of mixtures of butter fat and lard or tallow are slightly raised. Of course one must guard against falling into the error of attributing this to the presence of cocoa nut oil.

conclusions, the amount of supposed beef fat or lard be calculated with the help of the " rule of three."

The presence of cocoa nut oil in butter fat can also be detected by resolving the suspected butter fat into two fractions, with 95 per cent alcohol (in the manner described under " Lard," p. 699), and examining each fraction separately. This is illustrated by the following table due to *Arnold* [1] :—

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[1] *Zeits. f. Unters. d. Nahrgs. u. Genussm.*, 1907, xiv. 195. Cp. also table, p. 811, for pure butter fat.

Butter Fat containing 6 per cent Cocoa Nut Oil

	Butyro-refracto-meter at 40° C. "Degrees."	Saponifica-tion Value	Reichert-Meissl Value	Mean Molecular Weight of the Soluble Volatile Acids	c.c. N/10 KOH required for Insoluble Volatile Acids (Polenske's Method)	Iodine Value	Non-volatile Fatty Acids.			150 Grms. of Fat yielded Alcohol-soluble Portion.
							Butyro-refracto-meter at 40° C. Degrees.	Neutralisa-tion Value.	Iodine Value.	
										Grms.
I. Original Fat	48·1	226·2	23·4	103·0	2·65	40·0	31·3	219·8	43·6	...
II. Alcohol-soluble Fat	40·6	235·2	34·6	102·5	3·8	41·2	32·6	219·0	46·0	35·59
III. Alcohol-insoluble Fat	44·05	221·8	20·3	107·0	2·2	39·5	31·3	218·2	40·4	...

In conclusion it should be pointed out that the determination of the titration number of the insoluble volatile acids is usefully supplemented by the *phytosteryl acetate test,* which in its present form does not admit of quantitative interpretation, and which obviously becomes useless in case a margarine " earmarked " with sesamé oil or containing other vegetable oils and fats has been employed as an adulterant.

As a qualitative test, capable of indicating 5 per cent or 10 per cent of cocoa nut oil in butter fat, *Hinks* [1] recommends the following method : 5 c.c. of the melted and filtered fat are dissolved in 10 c.c. of ether in a test tube which is then corked up and placed in ice. In the course of half an hour a certain amount of solid glycerides will be found to have separated out, leaving a clear ethereal solution as an upper layer. The ether is poured on a filter and filtered rapidly. The ethereal solution is evaporated down on the water bath, the residual fat brought into a test tube and boiled with three to four times its volume of 96-97 per cent alcohol, in order to effect complete solution. On allowing the solution to cool to the ordinary temperature, most of the fat separates. The tube is placed next in water at 5° C., and kept at that temperature for fifteen minutes. The alcoholic layer is then rapidly filtered into another test tube, which is placed in ice, and kept at 0° C. for two or three hours. A flocculent deposit soon separates out. A portion having been withdrawn by the aid of a wide-mouthed pipette and placed on a slide, the crystals are examined microscopically under a magnification of 250-300, care being taken that the crystals are not broken by pressing the cover on the slide.

The glycerides deposited from pure butter fat form round granular masses, whereas cocoa nut oil yields fine needle-shaped crystals,[2] the forms of which can be readily observed even at a lower power than 250. In the case of a mixture of cocoa nut oil and butter fat, the deposit shows granular butter fat spheres side by side with numerous small, very fine, almost feathery crystals. These will generally be found attached to the butter fat granules, but sometimes they form clusters by themselves, their characteristic appearance being that of a mass of crystals growing from the side of the butter granules. *Hinks* states that the presence of 10 per cent of beef fat, cotton seed oil, or sesamé oil does not mask the presence of cocoa nut oil. Lard, however, does not interfere with this test, inasmuch as, treated by this process, lard yields stellate clusters of crystals which almost completely suppress the granular appearance of the butter fat crystals.

It should be noted that alcohol of less strength than 95 per cent is inadmissible, since butter fat has the tendency to assume crystalline form on separating from weaker alcohol. As the deposit is soluble in alcohol at the ordinary temperature, or at any rate loses its crystalline form, the microscopical examination must be conducted rapidly. If the temperature of the room should be somewhat high, the slide must

[1] *Analyst,* 1907, 160 ; cp. Césaro, vol. i. 366.
[2] This has also been observed by Morres (*Zeits. f. Unters. d. Nahrgs- u. Genussm.,* 1911, xxi. 432), who states that tallow, lard, and cocoa nut oil yield needle-shaped crystals.

be kept cool on a shallow glass dish containing clear lumps of ice.
Hinks concludes from several experiments that the feeding of cows

FIG. 16.—Pure Butter.   200 diam.

FIG. 17.—Pure Cocoa Nut Oil.   70 diam.

with cocoa nut cake does not interfere with this test.[1]   Further indica
tions are furnished by the microscopical slides reproduced here.[2]

[1] Cp., however, Lahache, *Journ. Pharm. Chem.*, 1903 (18), 338.
[2] These photomicrographs were prepared by E. R. Bolton.

'*Hoton*, who advocates the examination of butter in polarised light for the detection of cocoa nut oil, attaches too much importance to

FIG. 18.—Butter containing 5 per cent of Cocoa Nut Oil.   200 diam.

FIG. 19.—Butter containing 10 per cent of Cocoa Nut Oil.   200 diam.

the value of the microscopical appearance, as the whole art of butter manufacture is to prevent the crystallisation of the glycerides.

The butters obtained from cows fed on cocoa nut cake yield by alcoholic extraction glycerides simulating in their physical characteristics (refractive index, critical temperature, melting point, and microscopical appearance)[1] the glycerides obtained from cocoa nut oil. A grave miscarriage of justice may therefore occur if the analyst relies on these methods without having recourse to the phytosteryl acetate test.

A considerable number of other methods aiming at the detection of cocoa nut oil in butter fat are omitted here, for the reason that they do not furnish better results than can be obtained by the methods detailed above.[2]

Wauters recommends also the microscopic examination.

There may, however, be mentioned specifically two methods published recently by *Fendler*[3] as they embody new principles, although it is hardly likely that they will supersede the foregoing methods (viz. *Müntz and Coudon's*, and *Polenske's*). The first method is carried out in conjunction with the determination of the *Reichert-Meissl* value. *Fendler* dissolves those fatty acids from 5 grms. of butter fat, which are left after distilling off the volatile acids by the *Reichert* process, in 50 c.c. of petroleum ether, distributes 25 c.c. of the petroleum ether solution over 10 grms. of powdered and dried pumice, evaporates off carefully the petroleum ether, and treats with 50 c.c. of alcohol of the specific gravity 0·9123 at 15° C. (60 per cent by volume). An accurately measured portion of the alcoholic filtrate is then titrated with decinormal alkali, and thus the amount of c.c. of decinormal alkali required to saturate the non-volatile acids obtained by the described process is calculated. Pure butter fat requires under these conditions 40-48 c.c. of decinormal alkali, whereas palm nut oil requires 188 c.c. and cocoa nut oil from 192 to 205 c.c. The second method is based on the determination of the ethylesters boiling up to 300° C. For this second method cp. Vol. I. Chap. XII. For a method based on the solubility of the salts of the fatty acids cp. *Shrewsbury and Knapp*.[4]

If vegetable fats have been proved to be absent, and yet *Reichert-Meissl* values are obtained which leave a doubt as to the genuineness of the butter, then only admixture of *animal* fats can be suspected. In that case corroborative evidence should be sought in the determination of the saponification value.

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[1] *Falsifications et tribunaux*, by L. Leroux, Anvers, 1911, 93.

[2] Cassal and Gerrans, *Chem. News*, 1910, 190 ; Shrewsbury and Knapp, *Analyst*, 1910, 385 ; Blichfeldt, *Journ. Soc. Chem. Ind.*, 1910, 792.

[3] *Arbeiten a. d. Pharm. Inst d. Univ. Berlin*, 1908. The author states that the method has been worked out in 1903.

[4] *Analyst*, 1910, 385.

Saponification Value

As indicated in the table (p. 804) the mean saponification value of butter fat may be taken as 227.

Butter fats that yield abnormal *Reichert-Meissl* values also give abnormal saponification values, so that, to take an example, the saponification value may drop in the last stages of lactation to 218·5. It need hardly be repeated here that a " correct " saponification value alone is no proof of purity, for it is very easy to prepare mixtures of oleomargarine and cocoa nut oil having the mean saponification value of 227. The saponification value is best collated with the *Reichert* value. It has been shown above (p. 830) that when an abnormally high saponification value is associated with a low *Reichert* value, the presence of cocoa nut oil may be suspected. This, however, must not be looked upon as a rule, for *Olig and Tillman* [1] have shown that some undoubtedly genuine Dutch butters behave abnormally, in that high *Reichert-Meissl* values are associated with low saponification values, and *vice versa*. Thus, a butter of the *Reichert-Meissl* value 30·1 had the saponification value 224·6, and butter of the *Reichert-Meissl* value 26·1 had the saponification value 232·6. Abnormalities (if such a term be permitted) of this kind can only be due to the butter fat in the latter case containing a larger amount of myristic and lauric acid than in the former (see below).

It should not be forgotten that the saponification value depends on the vagaries of butter fat in the same manner as does the *Reichert-Meissl* value. Thus the above-mentioned abnormal butters, described under the heading of " Idiosyncrasy," gave the following values : —

Saponification Value.	Reichert-Meissl Value.	Mean Molecular Weight of the Insoluble Fatty Acids.
209·0	17·6	269·6
215·3	23·6	268·4
212·4	22·2	267·0

Butter fats having very high saponification values can be produced through feeding the cows with turnips or turnip leaves. Thus *Siegfeld* [2] obtained in experiments made with a herd of cows the following numbers :—

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1906, xi. 86.
[2] *Ibid.*, 1907, xiii. 517.

		Saponification Values.	
		Fed without Turnips.	Fed with Turnips.
Herd No. I.	. .	22*-235	238-241·4
Herd No. II.	. .	224-230	233-242·5
Herd No. III.	. .	230·6-233·1	233-243·5

Of less decisive importance for judging the purity of butter fat than the refractive index, the *Reichert-Meissl* value, the titration number of the insoluble volatile acids, and the saponification value, are the *specific gravity* and the *iodine value*. As some analysts still determine these characteristics in the examination of butter fat, either in order to obtain additional information or in the belief that these numbers constitute valuable criteria, they must be discussed here briefly.

SPECIFIC GRAVITY

J. Bell, who first proposed the determination of the specific gravity as a critical test for the examination of butter fat, chose the temperature of 100° F. = 37·8° C., and used an ordinary pear-shaped specific gravity bottle. In the examination of a large number of samples he found that the experimental values vary within the narrow limits of 0·911 and 0·913. In the subjoined table I collate the specific gravities of genuine butter fats and some other fats likely to be used as adulterants ; all numbers refer to the temperature of 100° F.

Specific Gravities of Butter Fats and Butter Adulterants

Kind of Fat.	Specific Gravity at 100° F. = 37·8° C. (water at 87·8 = 1).	Observer.
Genuine butter fat, 113 samples .	0·911-0·913	Bell
,, ,, ,, 357 ,,	0·9101-0·9130	Thorpe
,, ,, ,, 368 ,, .	0·9100-0·9200	v. Raijn
Mutton suet	0·90283	Bell
Beef suet	0·90372	,,
Oleomargarine	0·90136-0·90384	,,
Cocoa nut oil	0·910-0·9167	(cp. p. 645)
Lard	0·905-0·907	(,, 707)

From the last table, as also from the table given in Vol. I. Chap. V., the fact will be gathered that cocoa nut and palm nut oils, if present

in small quantities, cannot be detected by the specific gravity test alone. It further follows that a judiciously prepared mixture of cocoa nut oil with animal oils can be incorporated with butter fat, without being detected by an abnormal specific gravity number.

The importance which some analysts ascribe to the specific gravity test in judging butter fat is entirely unjustifiable. For this test would hardly lead to the detection of smaller quantities of an adulterant than 30 per cent, an amount which is revealed with the greatest ease by some of the foregoing methods. The over-estimation still accorded to the specific gravity test dates back to the time before the more modern methods had been discovered. Since these have come into vogue the specific gravity test has lost its importance, even as a corroborative test, for such gross adulterations as can be detected with the help of the specific gravity test alone are hardly practised nowadays.

The scientific explanation for the foregoing statements must be found in the fact that the slight influence which the few per cent of volatile fatty acids exercise, is completely outbalanced by slight variations in the composition of the remaining 94 per cent of insoluble fatty acids. This may be gathered from the numbers collated in the following table :—

Specific Gravity of Fatty Acids occurring in Butter Fat

Acid.				At ° C.	Specific Gravity.
Butyric .	.	.	.	20/4	0·9590
Caproic .	.	.	.	20/4	0·9274
Caprylic	.	.	.	20/4	0·9100
Capric .	.	.	.	40/4	0·8858
Lauric .	.	.	.	20/4	0·883
Lauric .	.	.	.	60/4	0·8642
Myristic	.		.	60/4	0·8584
Palmitic	.	.	.	62/4	0·8527
Stearic .	.		.	69·2/4	0·8454
Oleic .	.	.	.	11·8/4	0·8908
Oleic .	.	.	.	78·4/4	0·8540

Since the older literature contains a number of specific gravities to which reference is still being made, and as some countries stipulate in their laws and regulations (see p. 813) certain specific gravities, it may be found useful to have them here reproduced.

Violette[1] had stated that by means of a density determination alone butters may be rapidly sorted into three classes, viz. (a) those undoubtedly adulterated with margarine, or with arachis, sesamé, and poppy seed oils; (b) those open to suspicion; (c) those that may be considered practically pure.

In the light of the above given explanations this statement cannot be considered as correct.

[1] *Compt. rend.*, 1893 (117), 856.

Nothing is gained by determining the specific gravity *in vacuo* as *Violette* proposes. His numbers may, however, be recorded here :—

1 c.c. of	At 100° C. weighs *in vacuo* Grms.
Genuine butter . . .	0·86328-0·86425
Margarine	0·85766-0·85865

Skalweit, having found that the differences in the specific gravities of butter fats and of fats likely to be used as adulterants are greatest at 35° C., makes his determinations at this temperature. His results are given in the following table :—

Temperature.	Lard.	Margarine.	"Butterine."	Butter Fat.
°C.				
35	0·9019	0·9017	0·9019	0·9121
50	0·8923	0·8921	0·8923	0·9017
60	0·8859	0·8857	0·8858	0·8948
70	0·8795	0·8793	0·8793	0·8879
80	0·8731	0·8729	0·8728	0·8810
90	0·8668	0·8665	0·8663	0·8741
100	0·8605	0·8601	0·8598	0·8672

Other chemists prefer to determine the specific gravity at 100° C. (water at 15° C. = 1) ; the results recorded by the different observers agree in a satisfactory manner :—

Fat.	Koenigs.	Sell.	Allen.
			At 99° C., water 15·5=1.
Genuine butter . . .	0·866-0·868	0·866-0·868	0·867-0·870
Beef tallow	...	0·859-0·8605	...
Lard	...	0·860-0·8605	...
Oleomargarine	...	0·859-0·860	0·8585-0·8625
Adulterated butter . . .	0·859-0·865	0·864-0·865	...

The following specific gravities at 100° C., referring to water of 100° C. as unit, have been recorded :—

Specific Gravities at 100° C., *Water at* 100° C. = 1

Fat.	J. Bell.	Muter.	Allen.
Genuine butter fat .	0·9094-0·9140	0·9105-0·9138	0·9099-0·9132
Oleomargarine . .	0·9014-0·9038	0·903-0·906	0·902-0·905

Iodine Value

The *iodine value* is of very little importance in the examination of butter fats. This is shown, in the first instance, by the great variations in the numbers recorded in the table, p. 804. The amount of unsaturated fatty acids in a butter fat is greatly influenced by the kind of oil or fat given to the cow with the food. Since the amount of unsaturated fatty acids influences the refractometric constant (pp. 667, 819), the indications furnished by the iodine value are implicitly given by the refractometer numbers of the sample.

It should further be emphasised that all those influences which tend to reduce the amount of volatile fatty acids, apart from the influence of food, *pro tanto* increase the iodine value. Thus *Farnsteiner and Karsch* found the iodine value of butter fat obtained from cows that had been in milk for a long time as high as 49·7. Exceptionally high values—52·4 and 53·3—were observed by *Siegfeld.*[1]

Exceedingly low iodine values are obtained in the case of butter fats from cows fed on turnips and turnip leaves. *Siegfeld,*[2] as also *Amberger,*[3] observed as low iodine values as 22·5, 23·0, 23·4, 23·8, 23·9, 26·2, 26·5, 26·7 (see above).

Of still minor importance is the determination of the *insoluble fatty acids* (+ *unsaponifiable*), and of the *mean molecular weight* of the insoluble fatty acids.

The determination of the amount of *insoluble fatty acids* (see table, p. 806) is very rarely carried out at present in the examination of butter fat, since the test has been entirely superseded by the determination of the soluble volatile acids by *Reichert's* process. Moreover, the indications furnished by this test are too uncertain to admit of fixing, even approximately, the amount of any adulterant added. Even if normal numbers are found, they afford no proof of the purity of the sample. It should further be noted that the washing out of a larger or smaller amount of lauric acid from the insoluble fatty acids causes an appreciable error and corresponding uncertainty.

The determination of the mean molecular weight of the *insoluble fatty acids* has been proposed by several observers as a critical test, but inasmuch as the *Reichert* value and the saponification values furnish implicitly the same information, no further insight into the composition of the sample is gained. Some observers have even carried out complicated calculations, without noticing that they were introducing at the outset into their equations the result they hoped to obtain.

A synopsis of a number of determinations carried out with 357

[1] *Chem. Zeit.*, 1908, 506.
[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiii. 521.
[3] *Ibid.*, 1907, xiii. 614.

samples of English butter fats (*Thorpe* [1]) is reproduced in the following table :—

I.	II.	III.	IV.	V.	VI.	VII.
No. of Samples.	Butyro-rofracto-meter at 45° C. ("Degrees.")	Reichert-Wollny Value.	Specific Gravity at $\frac{37\cdot8°}{37\cdot8°}$ C.	Saponifica-tion Value.[2]	Insoluble Acids. Per cent.	Mean Molecular Weight of Insoluble Acids.
7	42·0	22·5	0·9101	219·65	90·1	266·9
17	41·5	23·5	0·9104	221·39	89·7	265·5
15	41·5	24·5	0·9108	223·24	89·4	265·0
27	41·3	25·5	0·9110	223·41	89·3	264·2
37	41·0	26·5	0 9113	225·39	88·9	261·9
51	40·6	27·5	0·9114	226·75	88·7	261·7
78	40·1	28·8	0·9118	228·32	88·4	260·9
56	40·1	29·5	0·9120	229·91	88·3	259·6
41	39 9	30·5	0·9123	231·43	87·9	260·1
18	39·7	31·3	0·9125	232·30	87·9	258·0
10	39·4	32·6	0·9130	232·58	87·7	257·8
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The numbers of the foregoing table must not be taken as expressing any fixed correlation or rule which can be applied straightway to the examination of any given sample, for the *mean values* naturally obliterate the irregularities which become apparent if the analytical data, which are summarised in the horizontal lines, are considered individually for each single sample. Moreover, some few samples, which had been examined in the course of this investigation, have been left out, as their data fell outside the range of the numbers which the remainder of the samples in the same horizontal line gave. For a complete study of this investigation the reader must be, therefore, referred to the analyses of the samples given in the Blue Book.[3] For the detection of lard and beef fat by *Polenske's* method, based on the relationship between the melting point and solidifying point, cp. Vol. I. p. 324.

Enough has been said in the foregoing lines to point out clearly that the "rapid" methods, although undoubtedly indicating in a given case whether a genuine butter or a grossly adulterated butter is under examination, fail in certain cases to allow of definite conclusions being drawn as to whether adulteration has taken place or not. The fundamental error of some analysts consists in resting satisfied with the performance of the "rapid" tests, which apply chiefly to the 6 to 7 per cent of volatile fatty acids, whereas the 94 per cent of insoluble fatty acids are not further investigated. A good deal of uncertainty is eliminated by performing the *phytosteryl acetate test*, as

[1] *Journ. Chem. Soc.*, 1904, 254.
[2] Calculated by the author from the saponification-equivalents given by Thorpe.
[3] Report of the Departmental Committee on Butter, 1904.

this test reveals unmistakably the presence of any vegetable oils and fats (cocoa nut oil, palm kernel oil) which may have been admixed to the butter as such, and also the presence of any *margarine containing vegetable oils*. It is therefore perfectly unnecessary to rely in the search for margarine on the assistance of the law-makers, who, in some countries, prescribe the compulsory addition of sesamé oil to margarine. In order to show how futile this palliative must be, it may be pointed out in the first instance that the adulterator, in defiance of the law, can easily prepare margarine to which no sesamé oil has been added. But even if, by careful supervision, a margarine maker could be prevented from omitting the sesamé oil, it is easy to circumvent the *Baudouin* test by employing colouring matters, which give a similar reaction to sesamé oil with hydrochloric acid alone. *Fendler*,[1] as also *Lewkowitsch* (before a Parliamentary Committee [2]), have shown that if it be attempted to wash out such colouring matters by treating the fat with hydrochloric acid, the treatment must be repeated so often that finally the fat no longer gives the *Baudouin* reaction, whether sesamé oil be present or not. As tho addition of colouring matters is not forbidden, it is obvious that the enforced addition of sosamé oil to margarine cannot be of any lasting help to the analyst. On the other hand, genuine butters have occurred which faintly gave the *Baudouin* colour test. On the strength of this test these butters would have been judged to have been adulterated with margarine. Tho colour reaction in these butters is due to part of tho chromogenetic substances of sesamé oil having passed into the milk fat of cows fed with sesamé cake. Although very many feeding experiments with sesamé cake have been carried out by a considerable number of observers, no concordant conclusions have been obtained. Whilst *Baumert and Falcke, Thorpe*,[3] and others have shown that the chromogenetic substance of sesamé oil does not pass into the milk, there are a number of other observers (*Vieth, Siegfeld*, a. o.) who deny this fact, and state that they distinctly obtained the sesamé oil reaction with butter made from the milk of cows that had been fed on scsamé cake. Considering the idiosyncrasy of animals and the difficulty of conducting physiological experiments, it was impossible to decide in favour of either of the two conflicting opinions. New light has been thrown on this question by *Engel*,[4] who has ascertained by a number of experiments that four to five hours after feeding with sesamé oil the *Baudouin* reaction became noticeable, whilst after another six to ten hours it could not be obtained, and that it reappeared again after a further four to five hours, then disappeared entirely. Since the feeding of milch cows with sesamé cake is on the increase in the north of Europe—in consequence of the legally prescribed addition of sesamé oil to margarine— genuine butter fat exhibiting the *Baudouin* reaction may occur more frequently than hitherto. In this connection it should be remembered

[1] *Chem. Revue*, 1905, 10.
[2] Report on the Butter Trade, July 1906.
[3] *Analyst*, 1898, 255; *Jahrbuch d. Chem.*, 1898, viii. 404.
[4] *Zeitschr. f. angew. Chem.*, 1906, 286.

that *König and Schluckebier* [1] have proved that the feeding of pigs with sesamé cake produces fats which give the *Baudouin* reaction distinctly.

In all those cases where butter is suspected of having been adulterated with margarine containing *vegetable oils*, the phytosteryl acetate test alone is sufficient to solve the problem. The only difficulty arises when animal fats *alone* have been employed for adulterating. As the manufacture of such animal fats is not subject to the compulsory addition of sesamé oil, it is obvious that here the sesamé colour reaction offers no assistance whatever. The adulterator has used this loophole to the full, and has brought into commerce butter adulterants consisting of animal fats only. The analyses of some such adulterants, which are sold under fancy names ("lardine," "butter improver," etc.), have been given above (p. 813).

In case adulteration with these animal fats has taken place none of the foregoing "rapid" methods, nor, indeed, all of them together, and not even the phytosteryl acetate test will be able to prove that an adulteration has taken place. Certainty can only be obtained by the further examination of the insoluble fatty acids. The author has commenced an examination of this kind, of which the outlines only can be given in the present incomplete state of the investigation. In the first instance the amount of *stearic acid* should be determined. Butter fat contains an insignificant amount of this acid, the author having obtained no more than 0·5 per cent. As oleomargarine yields about 20 per cent of stearic acid, and lard may yield up to 26 per cent, even small admixtures of beef fat or lard should be detectable. The author has further found that the determination of arachidic acid on the one hand and myristic acid on the other will prove of considerable assistance. In an investigation of this kind the "crude stearic acid," as obtained by the process described Vol. I. Chap. VIII., must not be looked upon, without further investigation, as being actually stearic acid. In some cases genuine butter fats gave, under the conditions described Chap. VIII., precipitates which might in a superficial examination have been judged to be stearic acid, whereas further investigation has shown in each case that a mixture of arachidic acid with myristic acid or a mixture of stearic, myristic, and arachidic acids was present (cp. also Chap. VIII.).

Should these investigations which the editor now has in hand not lead to a satisfactory result, the method of fractionally distilling the methylesters of the fatty acids (see Vol. I. Chap. XII.), although more laborious, may lead to decisive results (cp. also cocoa nut oil, p. 641).

Special colour reactions [2] for vegetable oils are hardly required in the examination of butter fat, and should only be used as corroborative tests. It should, however, be remembered that a positive *Halphen* test given by a butter fat does not prove the presence of cotton seed oil, since the chromogenetic body giving the *Halphen* reaction passes into the milk fat of cows fed on cotton seed cake.

[1] *Zeits. f. Unters. d. Nahrgs. u. Genussm.*, 1908, xv. 642.

[2] Cp. Ludwig and Haupt, *Zeits. f. Unters. d. Nahrgs. u. Genussm.*, 1907, xiii. 605 ; Merl, *ibid.*, 1908, xv. 529.

Since the critical temperature of dissolution (Vol. I. Chap. V.) has been embodied by the Belgian Government amongst the official tests of butter fat, the following numbers may be added to those given already Vol. I. Chap. V. :—

Critical Temperatures of Dissolution (Crismer)

	With Alcohol 0 7967 Specific Gravity (containing 0 9 per cent of water), at 15 5° C., in Open Tube.						With Alcohol 0 8195 (8 85 per cent of water), at 15 5° C , in Sealed Tube.	Differ- ence.
	a	b	c	d	e	f		
Butter								
1	54·8	54·8	54·8	54 6	54·3	53·8	100 5	45·7
2	54·5	54·5	54·5	54 2	..	.	100·5	46
3	57	57	57		...	...	103	46
4	54	54		...	...	...	100·5	46
5	50	50	...	..	...	...	105 5	45·5
6	56		...		...	.	102·5	46
7	56·5	52·2	.	.	...	...	102·5	46
8	52	52·4	56·5	52·4	51 2	..	98·2	45·7
Margarine and Mixtures								
1	78	78	...	...	...	.	124	46
2	72·2	72·2	..	...	.	.	118	45·8
3	72·5	.	.	...	...	..	118	45·5
4	78	...	.	...	...	.	123·8	45·8
5	69	..	. .	...	. .		115	46 0
6	63·8	..	...	...	..	.	109	45·2
Maize oil	70·5	...	...	...	.	...	...	...

It is curious to note that in the case of a rancid butter the number of c.c. of $\frac{n}{20}$ KOH required to neutralise 2 c.c. of butter fat (dissolved in 20 c.c. of absolute alcohol), when added to the figure representing the critical temperature of the acid butter, gives approximately the critical temperature of the neutralised butter.[1]

No. of Samples.	a Mean Critical Temperature of Acid Butter. °C.	b c.c. of $\frac{n}{20}$ normal Alkali required for 2 c.c.	c Critical Temperature of Neutralised Butter. °C.	d Difference. c − a.
3 at 80-90° C.	88·5	7·5	96·4	7·9
14 at 90-96° C.	93·5	4·8	98·2	4·7
69 at 96-102° C.	99·12	1·2	101·7	2·6
17 at 102-106° C.	103·9	1·0		

Ewers[2] states that this test is practically useless.

[1] *Bull. de l'Assoc. Belge des Chimistes*, 1897 (10), 453 ; *Analyst*, 1897, 158.
[2] *Milchw. Zentralbl.*, 1910, i. 154.

A large number of tests based on the behaviour of butter with fat *solvents* are omitted here as being entirely useless.[1] Since, however, *Valenta's* test, Vol. I. Chap. V., is still to some extent in vogue as a preliminary test, it may be described in the form employed by *Allen* :[2] 3 c.c. of the melted fat are poured into a test-tube, an exactly equal measure of glacial acetic acid is added, and the contents of the tube heated until complete solution takes place on agitation. The liquid is then allowed to cool spontaneously whilst stirred with a thermometer, and the temperature observed at which the solution becomes turbid. The turbidity temperatures found for genuine butter fats were from 56°-61·5° C., whereas those for margarine were 98°-100° C.

Jean does not regard the turbidity as a criterion, but estimates the volume of acetic acid dissolved by the fat (Vol. I. Chap. V.).

Some of his results are subjoined in the following table :—

Fat.						Acetic Acid dissolved. Per cent.
Pure butter		.	.	.	.	63·33
„	„	with 10 per cent of cocoa nut oil				66·66
„	„	„ 15	„		„ .	90
„	„	„ 28	„		„ .	96

It may be useful to describe here briefly the results obtained by the cryoscopic method devised by *Pailheret*.[3] This observer uses pure crystallisable benzene as a solvent, and lays stress on its freedom from thiophene. The temperature readings are taken from a delicate thermometer by means of a microscope. The solvent and the fat are weighed directly. *Pailheret* calculates the coefficient with the aid of the following formula :—If C equals the difference between the freezing point of the solvent and the freezing point of the solvent containing the fat, and P equals the weight of fat in 100 grms. of solvent, then the coefficient $A = \dfrac{C}{P}$. For dilute concentrations the variations of A are very marked. Where the concentration reaches 18-22 per cent the coefficient, however, becomes constant. For these concentrations $A = 0·0885$, whereas for margarine for the same concentrations $A = 0·0764$. This method can at best be used only as a "sorting test," and cannot in any way supersede the quantitative reactions.

For the method of detecting adulteration by means of the solubility of the barium and magnesium salts, the original paper by *Ewers*[4] must be consulted, all the more so as *Amberger*[5] states that the milk

[1] Hoton (*Bull. Soc. Chim. de Belgique*, 1904 (18), 147 ; *Revue intern. des falsific.*, 1906 (19), 115) showed that the solubility of butter in glacial acetic acid is not influenced by a larger or smaller proportion of glycerides of volatile acids.

[2] *Commercial Organic Analysis*, ii. 154.

[3] *Bull. Soc. Chim.*, 1909, 425. Cp. also Garelli and Carcano (Benzene), *Staz. sperim. agrar.*, 1893, 77 ; Partheil, *Arch. d. Pharm.*, 239, 358 ; Peschges, *Arch. d. Pharm.*, 239, 358 ; Pouret, *Bull. Soc. Chim.*, 1899, iii. 21, 738 ; Quartaroli (Acetic acid), *Staz. sperim. agrar.*, 1904 (37), 18 ; M. Raffo and G. Foresti, *Gazz. chim. ital.*, 1909 (39), ii. 441.

[4] *Milchw. Zentralbl.*, 1910, i. 154.

[5] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1911, xxi. 598.

yielded by cows at the end of the period of lactation, and particularly that from cows fed on cocoa nut cake, showed by *Ewer's* method apparent adulteration with 10 per cent or even more of other fats. This method, as also that of *Fendler*,[1] has been criticised by *Polenske*.[2]

With regard to a number of other methods, such as viscosimetric,[3] calorimetric,[4] and microscopical[5] examination, the reader must be referred to the original papers, as these methods have very little practical importance in the examination of butter fat, and are decidedly inferior to those described on the preceding pages.

STAG FAT

French—*Graisse de cerf.* German—*Hirschtalg.*
Italian—*Sego de cervo.*

A specimen of the fat from *Cervus elaphus* examined by *Klimont and Meisl*[6] yielded, on repeated crystallisation from acetone, needles melting at 62·5 to 63·5° C., which they identified as palmitodistearin.

The specimen examined by *Amthor and Zink*[7] had the acid value 3·5 in the fresh state, and 5·9 after keeping for one year.

Physical and Chemical Characteristics of Stag Fat

Specific Gravity.	Solidifying Point.	Melting Point	Saponification Value.	Iodine Value.	Reichert Value.	Refractive Index. Butyro-refractometer. "Degrees."	Observer.
At 15°C.	°C.	°C.	Mgrms. KOH.	Per cent	c.c. $\frac{1}{10}$ norm. KOH.	At 40°C.	
0·9670	39·40	51·52	199·9	25·7	1·66		Amthor and Zink
	48	49·49·5		20·5		44·5	Beckurts[8] and Oelze
0·9066 (at 50°)	47·5	48·0[9]	203·5	19·3			Klimont and Meisl

[1] *Zeitschr. f. öffentl. Chem.*, 1910 (16), 152.
[2] *Arb. a. d. Kais. Gesundheitsamt*, 1911 (38), 408.
[3] Killing, *Journ. Soc. Chem. Ind.*, 1895, 198; Wender, *Journ. Amer. Chem. Soc.*, 1895, 719. Cp also White and Twining, *Journ. Ind. and Eng. Chem.*, 1913, 568.
[4] *Journ. Soc. Chem. Ind.*, 1896, 560.
[5] Legros, *Revue intern. des falsific.*, 1906, 19, 159.
[6] *Monatsh. f. Chem.*, 1913, 1489.
[7] *Zeitschr. f. analyt. Chem.*, 1897, 4.
[8] *Arch. d. Pharm.*, 1895 (233), 429.   [9] Pohl's method.

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity.	Solidify-ing Point.	Melting Point.	Neutralisation Value.	Iodine Value.	Observer.
At 15° C.	° C.	° C.	Mgrms. KOH.	Per cent.	
0·9685	46-48	50-52	201·3	23·6	Amthor and Zink Beckurts and Oelze
		49·5			

Lesser known animal fats, see table on opposite page.

B. WAXES

I. LIQUID WAXES

Two representatives only of this class are known, viz. sperm oil and Arctic sperm oil. As regards origin, smell, taste, and some colour reactions, they are in many respects very similar to blubber oils ; so much so, that some writers classed them with the latter oils. On account of their different chemical composition the author separated them from the blubber oils, and this classification has now been adopted generally.

The liquid waxes contain **no** glycerides ;[1] they consist chiefly of compound esters of fatty acids and monovalent alcohols. They yield, therefore, on saponification, large quantities of " unsaponifiable matter." This characteristic readily serves to distinguish the liquid waxes from all other fixed oils. Whereas most fatty oils yield 95 per cent of fatty acids, the liquid waxes contain only from 60 to 65 per cent, the remaining 40 to 35 per cent being made up by monovalent aliphatic alcohols.

The liquid waxes are further readily distinguished from the fatty oils by their low specific gravities. It is notable that their viscosity is much less influenced by variations of temperature than is the case with fatty oils.

The liquid waxes absorb very little oxygen from the atmosphere, and therefore do not dry. On treatment with nitrous acid they give a solid or butter like elaïdin.

Some of the (fatty) blubber oils contain notable quantities of waxes, forming, as it were, a gradual transition from pure glycerides (seal oil) to the true liquid waxes.

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[1] This assertion may require qualifying, for if the statements of Fendler and of Dunlop (see p. 865) be confirmed, some sperm oils would appear to contain from 13 to 25 per cent of glycerides.

SPERM OIL

French—*Huile de cachalot* ; *Huile de spermaceti.*   German—*Walratöl* ;
Pottwaltran.   Italian—*Olio di spermaceti.*

For tables of characteristics see p. 868.

Sperm oil is obtained from the head cavities and from the blubber
of the sperm whale, or cachalot, *Physeter macrocephalus*, L.   On " try-
ing " (cp. " Whale oil," p. 456) the sperm whale on board ship, the head
and body blubbers are kept separate, since the oil from the head is
worth more than that from the body.[1]   The oils obtained from the head
matter and from the body blubber differ considerably in appearance.
The former oil, when first taken from the head of the whale, is clear and
limpid " brain oil," but after a short time thickens and hardens to a
white mass.   The latter (body oil) is, in its fresh state, a light straw-
coloured oil.   The oils are kept separate on board ship, but when re-
ceived at the refineries they are generally mixed in their natural pro-
portions, viz. one-third head oil and two-thirds body oil, and together
submitted to the processes for separating the oil from the spermaceti.

Sperm whales yield from 5 to 145 barrels of crude oil ; the average
yield for the cows is about twenty-five to thirty, and for the bulls
seventy-five to ninety.   (Each barrel weighs about 230 lbs.)

In the refineries the crude sperm oil is allowed to stand in refrigerating
chambers from ten to fourteen days at a temperature of 32° F.   The
partly solidified mass is then subjected to hydraulic pressure.   The
clear oil thus obtained is known as " winter sperm oil " ; it will not
congeal at 38° F., which is at present the usual commercial standard.
Oils of 32° or 23° F. " cold-test " have also been prepared.   The tend-
ency is to produce oils of somewhat high cold-tests, since the lower the
temperature at which the congealed oil is pressed the smaller is its yield.
The amount of " winter sperm oil " of 38° F. " cold-test " is about 75
per cent of the crude oil.   When 32° F. " cold-test " was the commercial
standard, the yield of " winter sperm oil " was about 67 per cent.   The
" winter sperm oil " is usually bleached.

After the " winter sperm oil " has been pressed out, there remains
in the press-bags a solid mass of brownish colour, which is again sub-
mitted to pressure at a higher temperature (about 50° to 60° F.), whereby
the oil known as " spring sperm oil " is obtained.   This congeals at
50° F. to 60° F.   The quantity of " spring sperm oil " is about 9 per cent
of the crude oil.

The press-cakes are stored for several days at a temperature of about
80° F., and in the course of a week are trimmed by revolving knives
and again submitted to a high pressure in hydraulic presses.   Thereby
a third grade of oil, " taut-pressed oil," is obtained, which solidifies at a
temperature of 90° to 95° F.   The quantity of oil of this grade is about
5 per cent of the crude oil, so that from the crude sperm oil a total of
89 per cent of refined oil is obtained.   The residue in the press-cloths is
crude spermaceti of a brown colour, which melts at a temperature of
110° to 115° F.

[1] About one to two cents per gallon.

The following statistical data have been published by the United States Government :—

Year.	Total production. Barrels (230 lbs.).	Exports. Barrels (230 lbs.).
1860	78,708	82,792
1861	68,932	37,547
1862	55,641	27,976
1863	65,055	13,366
1864	64,372	45,000
1865	33,242	20,158
1866	36,663	10,630
1867	43,433	25,147
1868	47,174	13,916
1869	47,936	13,645
1870	55,183	22,773
1871	41,534	22,156
1872	45,201	24,844
1873	42,053	16,238
1874	32,203	18,675
1875	42,617	22,802
1876	39,811	23,600
1877	41,119	18,047
1878	43,508	82,769
1879	41,308	11,843
1880	37,614	12,283
1881	30,600	16,600
1882	29,844	13,006
1883	24,595	13,996
1884	22,099	5,143
1885	24,203	7,554
1886	23,312	3,118
1887	18,873	4,955
1888	16,265	1,345
1889	18,727	5,823
1890	14,480	2,000
1891	13,015	3,218
1892	12,944	1,787
1893	15,253	1,165
1894	16,333	1,720
1895	16,585	1,225
1896	15,124	215
1897	15,050	230
1898	12,520	1,952
1899	11,903	550
1900	18,525	1,100
1901	14,910	...
1902	21,970	470
1903	18,109	...
1904	17,050	...
1905	12,985	...
1906	15,955	515
1907	13,490	...
1908	14,075	...
1909	16,755	..
1910	18,078	..
1911	21,915	...
1912	17,495	...

Refined sperm oil is a pale yellow, thin oil, almost free from odour.

Hoffstätter's statement that sperm oil contains glycerides has been shown by *Allen* and by the author to be erroneous. Possibly *Hoffstätter* [1] examined an oil mixed with porpoise oil, since he found in his specimen valeric acid as well as glycerol.

More recently, however, *Fendler* [2] detected in a genuine sperm oil still containing spermaceti and having the saponification value of 150·3, 1·32 per cent of glycerol (confirmed by the acrolein test). It will be noted that the saponification number of this sperm oil is extremely high, higher than any numbers recorded by previous observers. Some Japanese sperm oils also appear to give high saponification values, and the author found in a brain oil from Japan the saponification value 150·5, and in a " skin " oil, also from Japan, the saponification value 137·1. These samples yielded 1·87 per cent and 2·30 per cent of glycerin respectively. *Dunlop* [3] also states that he found in a sperm oil from the body and in two oils from the head the following percentages of glycerol (by means of the acetin method):—1·36, 1·53, and 2·51 respectively. The saponification values of these oils were, in the same order, 122·0, 140·2, 144·4. He only states that the samples were obtained from " reliable sources."

The sperm oil fatty acids, a few characteristics of which are given p. 868, appear to belong to the oleic series, as is shown by their iodine value, and by their property of yielding elaïdin with nitrous acid. The nature of the acids is as yet unknown. *Hoffstätter's* earlier statement that the fatty acids consist chiefly of physetoleic acid stands in need of confirmation. *Bull* isolated from two specimens of sperm oil 7·53 per cent of liquid fatty acids, which had respectively the neutralisation values 183·4 and 187·9, and the iodine values 130·3 and 159·5.

Fendler found in a specimen of sperm oil, still containing spermaceti, 14·22 per cent of solid and 85·78 per cent of liquid fatty acids. The solid acids melted at 32·2° C. and had the neutralisation value 242·5. The liquid fatty acids had the neutralisation value 228·7 and the iodine value 75·6. An attempt to resolve the liquid fatty acids into different fractions by distillation under diminished pressure did not lead to definite results. The highest iodine value (fraction No. 4) was 92·0. The following table reproduces *Fendler's* results :—

Fraction No.	Boiling Point. °C.	Pressure (mm.).	Approximate Yield (c.c. from 100 c.c.).	Iodine Value.	Neutralisation Value.	Mean Molecular Weight.
1	165-185	25	8	48·5	274·8	204·4
2	185-200	,,	30	75·3	256·5	218·9
3	200-210	,,	10	87·7	241·7	232·3
4	210-220	,,	10	92·0	230·4	243·8
5	220-225	,,	10	90·0	223·4	251·4
6	225-235	,,	5	90·8	218·9	256·6
7	235-250	,,	5	78·3	213·7	262·8
8	250-260	50	4	91·6	205·7	273·0
9	260-265	,,	10	89·3	195·4	287·4

[1] *Liebig's Annal.*, 1854, 91, 177.   [2] *Chem. Zeit.*, 1905, 555.   [3] *Journ. Soc. Chem. Ind.*, 1908, 63.

The fractions were liquid at the ordinary temperature; only the three last fractions showed signs of crystallisation at the temperature of the freezing point of water.

Walker and Warburton[1] obtained in the author's laboratory from two specimens of sperm oil 2·5 and 3·7 per cent respectively of ether-insoluble brominated glycerides (Vol. I. Chap. VIII.). The insoluble fatty acids gave in the bromide test 2·05 per cent of ether-insoluble brominated acids. *Procter and Bennett*[2] obtained as much as 6·3-6·5 per cent of ether-insoluble bromides. These high figures were not confirmed by *Dunlop*, who found, in good agreement with the results obtained by *Walker and Warburton*, 1·13-2·3 per cent ether-insoluble brominated acids.

The author obtained from two samples of Japanese skin oil 2·25 and 1·06 per cent of insoluble brominated fatty acids, and from two samples of Japanese brain oil 1·12 and 0·63 per cent respectively. These bromides behaved like clupanodonic octobromide in the melting point test.

Lewkowitsch[3] found the acetyl values of three samples of northern, "northern best," and southern sperm oil, 4·49, 6·43, and 5·25 respectively.

The nature of the alcohols of sperm oil is also unknown. The author[4] tried to resolve the mixed alcohols into their several constituents by fractional distillation of both the alcohols themselves and of their acetates, but hitherto these experiments have not led to any definite result, beyond proving that neither dodecatyl nor pentadecyl alcohol is present, and that the sperm oil alcohols belong for the most part, if not wholly, to the ethylene series, the higher members of which have been hitherto unknown.

This will be readily seen from the following table, giving the saponification values of the acetates of the five fractions into which the total amount of acetates were resolved, and the iodine values of the corresponding alcohols themselves. For the sake of comparison the theoretical numbers are given for alcohols, the presence of which might be expected.

Alcohols from Sperm Oil.	Saponific. Value of Acetate	Iodine Value of Alcohol.
1st fraction . . .	190·2	46·48
2nd ,, . . .	183·8	63·30
3rd ,, . . .	180·7	69·80
4th ,, . . .	174·4	81·80
5th ,, . . .	161·4	84·90
Alcohol $C_{16}H_{32}O$ (unknown)	199	106·6
,, $C_{18}H_{36}O$ (unknown)	180	94·8
,, $C_{20}H_{40}O$ (unknown)	166	85·8

On heating[5] with soda-lime the alcohols were for the most part converted into fatty acids, only 4·6 per cent of unchanged alcohol being recovered; these crude fatty acids had the acid value 181·7, and melted at 38°-40° C.

[1] *Analyst*, 1902, 237.   [2] *Journ. Soc. Chem. Ind.*, 1906, 798.   [3] *Analyst*, 1899, 821.   [4] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 134.   [5] *Ibid.*, 1896, 41.

A more recent examination by the usual methods (*Dunlop*) led to the following numbers:—

	Cold Test °C.	Sp. gr. at 15·5° C.	Wax Alcohols, etc. Per cent.	Iodine Value. (Wijs.)	Saponification Value.	Butyro-refractometer. "Degrees." at 25° C	Free Acid as Oleic Acid. Per cent.	Wax Alcohols, etc.			
								Iodine Value. (Wijs.)	Melting Point °C.	Butyro-refractometer. "Degrees." 25° C.	40° C.
Sperm oil from "head matter"	9·5	·8779	42·28	76·30	140·2	49·7	4·60	60·43	32-32·5	...	35·0
,, ,, ,, "body matter"	8·5	·8772	42·14	92·85	124·8	54·8	1·42	83·17	24·5-25·5	47·0	39·0
,, ,, ,, "head matter"	7	·880	41·16	70·35	144·4	50·0	1·39	53·7	31·5-32·5	...	35·0
,, ,, ,, "body matter"	7	·8757	44·30	87·90	122·0	54·6	1·07	79·77	23-24	47·0	...
Southern sperm oil	...	·8791	41·16	84·35	129·7	54·6	1·16	68·5	26·5	45·7	37·7
,, ,, ,,	...	·8798	39·20	84·37	129·0	...	2·53	69·37	...	...	...

Physical and Chemical Characteristics of Sperm Oil

Specific Gravity		Saponification Value		Iodine Value		Reichert-Meissl Value		Fatty Acids		Alcohols		Maumené Test		Refractive Index	
°C	Observer	Mgrms. KOH	Observer	Per cent	Observer	c.c. norm. KOH	Observer	Per cent	Observer	Per cent	Observer	°C	Observer	At 20° C.	Observer
15	0·8799-	123·4	Deering, Stoddart,	84	Archbutt	0·60 [2]	Fendler	60·64	Allen	39·,	Allen	51	Archbutt	1·4646-	Harvey [1]
	Bull	147·4	Allen	81·3	Thomson and Ballantyne					41·5,	Lewkowitsch			1·4655	Bloxam
15·5	0·8835				M'Ilhiney					41				1·4651	
	0·875-	125·2 [3]	Lewkowitsch		Bull					37·41	Thomson and Ballantyne				
	Allen			86·5 [4]								Specific. Temp. Reaction		Oleo-refractometer.	
″	0·8908	127·9	″	85·7,						39·6	Fendler			"Degrees."	Observer.
	Thomson and Ballantyne	132·6 [5]	Archbutt and Deeley	90·1						39·2,	Dunlop	100	Thomson and Ballantyne	−12 to −17·5	Jean
	Dunlop	12·9	Bull	70·4,	Dunlop					41·3				−13	A. and D.
20	0·8757-	129·2-	Fendler	92·9										Butyro-refractometer.	
99 (water at 15·5 =1)	0·880 [6]	136·9,	Allen											°C.	"Degrees."	Observer.
	0·8781 [7]	132·5,												25	49·7-54·8	White Dunlop
	0·8303	150·3 [6]												40	>46·2	White
15	0·87867 [7]	122·,	Lewkowitsch	96·86	Lewkowitsch			62·67	Lewkowitsch	43·09	Lewkowitsch	48·45	Bloxam			
15·5	0·8797	144·4	Bloxam	96·4	Bloxam			59·07	Bloxam	41·09	Bloxam					
		126·8														
		125·9														

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Specific Gravity		Solidifying Point		Titer Test		Melting Point		Mean Molecular Weight		Iodine Value	
At 15·5° C.	Observer	°C.	Observer	°C.	Observer	°C.	Observer		Observer	Per cent	Observer
0·899	Allen	16·1	Archbutt and Deeley	11·1-11·0	Lewkowitsch	21·4	Archbutt and Deeley	281·294	Allen	88·1	Williams
						13·3	Williams	305	Williams	83·2-85·6	Lewkowitsch
								287·7	Fendler [6]	98·74	Bloxam

[1] Nine samples.　　[2] Chem. Zeit., 1905, 555.　　[3] Southern sperm oil.　　[4] Calculated from bromine addition value 54·54 (bromine substitution value being 1·04).　　[5] Northern sperm oil.　　[6] The specimen had the acid value 18·2 and still contained spermaceti; the solidifying and melting points of this specimen are given respectively as 15·5 and 18° C.　　[7] Southern sperm oil yielding 1·27 per cent of glycerin, 2·87 per cent of insoluble brominated fatty acids, and showing a violet colouration in the sulphuric acid test.

Physical and Chemical Characteristics of Alcohols (Unsaponifiable Matter)

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
22-23·4	Lewkowitsch	25·5-27·5	Lewkowitsch	64·6-65·8	Lewkowitsch

Commercial sperm oil contains only small quantities of free fatty acids. In the following table a few numbers are recorded :—

No	Sperm Oil	Free Fatty Acids, as Oleic Acid Per cent	Observer.
1	Best quality, cold bagged .	1·46	Deering
2	Second, "hot pressed" . .	2·11	„
3	Intermediate quality . .	0·75	„
4	Oil of good quality . .	2·11	„
5	Oil of doubtful quality .	0·55	„
6	„ „ „ . .	1·21	„
7	Oil of bad quality . . .	2·06	„
8	„ „ . . .	2·64	Thomson and Ballantyne

Sperm oil is a valuable lubricating oil for spindles and light machinery, on account of its slight tendency to " gum," and because the viscosity does not decrease so rapidly with the increase of temperature as is the case with other lubricating oils (see Vol. III.). A sample of sperm oil examined in the writer's laboratory required in *Redwood's* viscosimeter 146·5 seconds at 70° F. (cp. also Vol. I. Chap. V.).

The comparatively high price of sperm oil invites adulteration with fatty oils or hydrocarbon oils. The detection of these adulterants is an easy task. Admixture with Arctic sperm oil, the physical and chemical characteristics of which are almost identical with those of sperm oil, is, however, very difficult to detect.

The *specific gravity* of sperm oil being very low, a high density of a sample would point to the presence of fatty oils. Mineral oils of the same specific gravity cannot of course be detected by the determination of this characteristic. However, a mixture of fatty oils with hydrocarbon oils, to meet the specific gravity, would require oils of so low a specific gravity that the flash point of the resulting oil would be very low indeed. The flash point of sperm oil lies in the neighbourhood of 450° F.

The *low saponification value* of most specimens of sperm oil obtained until recently, furnished a ready means of detecting added fatty oils, such as rape oil, blubber oils, etc. As, however, a judiciously added quantity of mineral oil may compensate the increase of the saponifica-

tion value due to this cause, an oil of apparently normal saponification value may result. In fact, *Lobry de Bruyn* [1] has shown that oils occur n commerce consisting of a mixture of sperm, blubber, and mineral oils. It should, however, be noted that *Fendler,* as also *Dunlop,* found the exceptionally high saponification values 150·3, 140·2, and 144·4 for genuine sperm oil. The saponification value alone cannot, therefore, be considered as finally proving the purity of the sample.

The presence of notable amounts of hydrocarbons can be proved with certainty by examining the unsaponifiable matter by means of acetic anhydride,[2] as detailed Vol. I. Chap. IX. The estimation of the amount of glycerol and calculation therefrom to fatty oil would seem to be no longer admissible, since *Fendler and Dunlop* found notable amounts of glycerol in sperm oils looked upon by them as genuine (cp. footnote, p. 862).

Colour reactions are hardly required in the examination of sperm oil. The colour test with sulphuric acid can no longer be accepted as an absolute proof of the presence of liver oils, since within the last few years sperm oils of undoubted purity have been coming on to the market which give positive reactions. The readiest way to detect liver oils is to determine the iodine value of the sample and the yield of ether-insoluble brominated fatty acids.

ARCTIC SPERM OIL—BOTTLENOSE OIL

French—*Huile de rorqual rostré.* German—*Döglingöl, Entenwalöl.* Italian—*Olio di spermaceti artico.*

For tables of characteristics see p. 873.

Arctic sperm oil is chiefly obtained from the bottlenose whale, *Hyperöodon rostratus* and *H. diodon* (*bidens*). The principal places where these species are caught are along the edges of the ice-fields of Northern Europe, between Bear Island and Iceland. Like the sperm whale the bottlenose whale contains in the cavity of the head a certain amount of oil which yields spermaceti. The quantity of crude oil obtainable from the bottlenose whale varies from 4 to 12 barrels, averaging about 8 barrels. The oil is usually "tried" out on board ship. The blubber is sometimes kept until the oil runs out spontaneously, when the oil naturally acquires a dark colour and becomes slightly hydrolised. Such an oil, after removing the spermaceti, of which it contains about 10 per cent, must then be refined with soda before it is fit for use as lubricating oil. The blubber oil is, as a rule, darker in colour than sperm oil; but the deodorised Arctic sperm oil of commerce so closely simulates sperm oil, that it is practically impossible to

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[1] *Journ. Soc. Chem. Ind.,* 1894, 426.

[2] Absolute alcohol must not be used for the detection of mineral oil in the alcohols, as an ethyl alcoholic solution of the sperm alcohols, even if spirit of 0·8345 specific gravity be used, is capable of holding considerable quantities of mineral oil in solution (cp. Nash, *Analyst,* 1904, 3).

distinguish the two oils by mere chemical examination. In the elaïdin test Arctic sperm oil yields a much softer elaïdin than sperm oil.

In commerce, however, these two oils are readily distinguished by their taste. On account of its more pronounced tendency to " gum," Arctic sperm oil is lower in price than sperm oil.

Scharling, writing in the year 1848, states that Arotic sperm oil is the dodecatylester of doeglic [1] acid. It hardly needs pointing out that this statement requires confirmation. In a more recent examination *Bull* obtained from two specimens of Arctic sperm oil 5·07 per cent and 3·65 per cent of fatty acids, which had the neutralisation values 154·6, 195 (?), and the iodine values 125·6, 121·2 respectively. The iodine values of these acids are lower than the iodine values of the corresponding acids obtained from sperm oil, whereas, considering the more pronounced gumming properties of Arctic sperm oil, the reverse would have been expected. *Lewkowitsch* [2] found the acetyl values of two Arctic sperm oils 6·35 and 4·12.

The amount of free fatty acids in two samples of Arctic sperm oil examined by *Deering*, and *Thomson and Ballantyne*, was 2·11 and 1·97 per cent respectively. *Bull* found in two specimens 0·9 and 3·4 per cent of free fatty acids.

With regard to the flash point of the oil see Vol. I. Chap. V.

A more recent examination, by the usual methods, of two specimens of Arctic sperm oil (*Dunlop* [3]) gave the following numbers :—

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[1] Bull is of the opinion that " doeglic acid " is a mixture of oleic and gadoleic acids. *Berichte*, 1906, 3570.

[2] *Analyst*, 1899, 321.   [3] *Journ. Soc. Chem. Ind.*, 1908, 63.

[TABLE

	Sp. gr. at 15.5° C.	Wax Alcohols, etc. Per cent.	Iodine Value. (Wijs.)	Saponification Value.	Glycerol. Per cent.[1]	Ether-insoluble Brominated Glycerides. Per cent.	Butyro-refracto-meter at 25° C. "Degrees."	Free Acid as Oleic Acid. Per cent.	Wax Alcohols, etc. Iodine Value. (Wijs.)	Melting Point °C.	Butyro-refractometer. "Degrees." 25° C.	Butyro-refractometer. "Degrees." 40° C.
1. Arctic sperm (bottlenose) . .	·8806	38·02	88·75	129·0	2·56	3·04	55·2	0·73	80·35	23·5-24	46·7	38·7
2. Arctic sperm (bottlenose) . .	·8736	39·22	82·80	124·8	2·26	...	55·3	1·43	69·4	23	46·2	38·2

[1] Having regard to the other characteristics of the oil, these numbers appear so high that they should be accepted with reserve.

Physical and Chemical Characteristics of Arctic Sperm Oil

Specific Gravity		Saponification Value		Iodine Value		Reichert Value		Insoluble Fatty Acids		Alcohols.		Manmené Test.		Refractive Index. Oleo-refractometer.	
At °C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. norm. KOH	Observer.	Per cent.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees."	Observer.
15	Bull	126	Deering	77.41	Mills and Akitt	1.4	Allen	61-65	Allen	37.41	Allen	42	Archbutt	−13	Archbutt and Deeley
15.5	Lewkowitsch	123.	Archbutt	80.4	Archbutt					36.32	Thomson and Ballantyne	41-47	Allen		
,,	Thomson and Ballantyne	134	Thomson and Ballantyne	82.1	Thomson and Ballantyne					31.7- 42.8	Lewkowitsch	Specific Temp. Reaction.			
,,		130.4		84.5	Lewkowitsch					34.11- 34.9	Archbutt and Deeley				
93-99 (water 15.5=1)	Allen	128.4 135.9 121.5 122.3	Lewkowitsch Bull	67.1- 79.7	Bull					39.7 41.1 42.0	,, Bull	93	Thomson and Ballantyne		

Physical and Chemical Characteristics of the Insoluble Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
10.7	Archbutt and Deeley	16.1 10.3-10.8	Archbutt and Deeley Lewkowitsch	82.2-83.8	Lewkowitsch
Titer Test					
8.3-8.8	Lewkowitsch				

1 Calculated from the bromine value.

Physical and Chemical Characteristics of the Alcohols (Unsaponifiable Matter)

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
21·7-22·0	Lewkowitsch	23·5-26·5	Lewkowitsch	64·8-65·2	Lewkowitsch

The change which Arctic sperm oil undergoes on blowing with air is detailed in the following table, due to *Procter and Holmes* [1] :—

Hours.	Specific Gravity.	Refractive Index.	Iodine Value.
0	0·885	1·4670	80·0
3	0·887	1·4672	76·0
6	0·887	1·4672	76·0
9	0·887	1·4673	76·0
12	0·887	1·4673	74·0
15	0·888	1·4675	74·0
18	0·890	1·4676	73·0
21	0·891	1·4677	71·0
24	0·892	1·4677	71·0

II. SOLID WAXES

1. VEGETABLE WAXES

Vegetable waxes (the exudations of plant leaves) seem to be widely spread over the vegetable kingdom, though they mostly occur in small quantities. With the exception of carnaüba wax, flax wax, gondang wax, and pisang wax, the nature of these waxes [opium wax (Chap. I. " Waxes "), palm wax, getah wax, ocotilla wax, cotton seed wax, sugar cane wax,[3] esparto wax, etc.] has been but little studied (cp. also Étard, *La Biochémie et les chlorophylles*).

A specimen of " chlorophyll wax " (the wax accompanying chlorophyll) examined by the author melted at 73° C., and was found to consist entirely of " unsaponifiable matter " representing a higher alcohol.

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[1] *Journ. Soc. Chem. Ind.*, 1905, 1287.   [2] Original oil.

[3] It is stated that 1 ton of sugar cane yields 1 lb. of wax, which is described as melting at 82° C., solidifying at 80° C., and having the specific gravity 0·961. The chemical composition of sugar cane wax is unknown, and the statement made by earlier writers that it consists of a saturated alcohol of the formula $C_{24}H_{50}O_2$ (" cerosin ") stands in need of confirmation.

On boiling with acetic anhydride it gained 6·3 per cent in weight. The saponification value of the acetate was 134·6. The recovered alcohol melted at 79-80° C. and had the iodine value 5·8.

With regard to Montan Wax (Lignite Wax), Sea-weed Wax, and Peat Wax, cp. Vol. III. " Candle Manufacture."

CARNAÜBA WAX

French—*Cire de carnauba.*   German—*Carnaubawachs, Cearawachs.*
Italian—*Cera di carnauba.*

For table of characteristics see p. 877.

Carnaüba wax is exuded by the leaves of *Corypha cerifera,* Virey (*Copernicia cerifera,* Mart.), a palm indigenous to tropical South America.[1] This palm occurs in the States of Bahia, Pernambuco, Rio Grande do Norte, Piauhy, Ceara, Maranhao, and Matto Grosso. It is especially plentiful in the province of Ceara, Brazil. The wax is gathered during the months of September to March by pulling off the leaves before they have fully opened and drying them for two or three days in the sun. During these six months the leaves can be cut twice a month, a good worker cutting about 1500 leaves per day. About 2000 to 4000 leaves are required to produce 16 kilos. of wax. The white powdery mass covering the surface of the leaves is first brushed off, then scraped off, and thrown into boiling water. After fifteen to twenty minutes the wax collects on the top as a dough-like mass, and is taken off after cooling.

The crude wax, as obtained from the plant, is dirty greenish, or yellowish; it is very hard, and so brittle that it can be readily powdered.

The chief ports from which crude carnaüba wax is shipped to Europe are Ceara, Pará, Paranguá, Pernambuco, Rio de Janeiro, and St. Luiz de Maranhas. The chief places of import in Europe are Hamburg and Liverpool. Considerable quantities are also shipped to the United States. The total exports from Brazil are given in the following table :—

Year.	Kilos.	(Paper) Milreis.
1905	1,895,757	3,291,126
1906	2,559,247	6,316,078
1908	2,592,027	3,871,849
1909	3,041,683	4,057,499
1910	2,680,986	4,308,819
1911	3,214,152	5,856,606
1912	3,099,102	5,450,681

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[1] Cp. Brande, *Philos. Trans.*, 1811, part ii.

During the first six months of 1913 the exports from Brazil reached the record figure of 2403 metric tons, valued at £266,000.

The prices of carnaüba wax are subject to great fluctuations, as the small quantities produced lend themselves readily to market speculations.

The crude carnaüba wax is refined by remelting over water and removing the dirt. In the trade the following qualities are differentiated : "yellow flor, yellow prime, yellow medium, grey fatty, and chalky." These two latter names correspond to the German " Fettgrau " and " Kurantgrau." Some qualities are bleached by filtering over bleaching earth, etc., and yield the " yellow carnaüba wax " of commerce. It should, however, be noted that in order to facilitate the process of bleaching, the carnaüba wax is always mixed with a certain amount of paraffin wax. This of course lowers the melting point, hence the bleached carnaüba wax of commerce is much softer than genuine carnaüba wax, and melts at about 60° C. Bleached commercial carnaüba wax rarely has a higher melting point than 74° C., which would correspond to about 5 per cent of added paraffin wax. When the percentage of paraffin wax is high the bleached commercial wax is almost white. Some makers melt ceresin with the crude carnaüba, and use bichromate of potash and sulphuric acid as bleaching agents.

Carnaüba wax dissolves completely in ether and in boiling alcohol ; on cooling, a crystalline mass, of the melting point 105° C., is deposited from the alcoholic solution. On ignition, commercial samples of carnaüba wax yielded 0·43 per cent of ash.

By subjecting carnaüba wax to repeated fractional crystallisation, *Liebermann*[1] obtained crystals of the melting point 92° C. simulating felted paper in appearance and having no lustre (differing from cochineal wax). The melting point could not be raised by further recrystallisation.

Carnaüba wax was formerly looked upon as consisting, like beeswax, chiefly of melissyl (myricyl) cerotate and small quantities of free cerotic acid and melissyl (myricyl) alcohol ; the latter is easily removable by cold ethyl alcohol. *Stürcke*,[2] who carried out a very complete research into the chemistry of carnaüba wax, maintains that free cerotic acid is absent. The definite acid value, however, found by other observers, undoubtedly points to its presence. According to *Stürcke*, the following are the constituents of carnaüba wax :—

(1) A hydrocarbon, melting at 59°-59·5° C. (2) An alcohol of the composition $C_{26}H_{54}O$ (ceryl alcohol), melting at 76° C. (3) Myricyl alcohol, $C_{30}H_{62}O$, melting at 90° C.[3] (4) A dihydric alcohol $C_{25}H_{52}O_2$ (cp. Vol. I. Chap. III.), melting at 103·5°-103·8° C. (5) An acid $C_{24}H_{48}O_2$ (carnaübic acid), melting at 72·5° C. (6) An hydroxy acid $C_{21}H_{42}O_3 = C_{19}H_{38} \begin{matrix} CH_2OH \\ COOH \end{matrix}$, or its lactone $C_{19}H_{38} \begin{matrix} CH_2 \\ CO \end{matrix} \bigg\rangle O.$[4]

[1] *Berichte*, 1885, 1979.　　　　　　　　[2] *Liebig's Annal.* 223, 283.

[3] Gascard (*Journ. Chem. Soc. Ind.*, 1893, 955) assigns to it the formula $C_{31}H_{64}O$.

[4] Schreiner and Shorey found in a black clay deposit of North Dakota an acid $C_{21}H_{42}O_3$ (*Chem. Zeit.*, 1909, 1339).

Physical and Chemical Characteristics of Carnaúba Wax

Specific Gravity			Solidifying Point		Melting Point		Acid Value		Saponification Value	
	°C.	Observer.	°C.	Observer.	°C.	Observer.		Observer.	Mgrms. KOH.	Observer.
0·999	15	Maskelyne	...	...	84·1	Mills and Akitt	4	Hübl	79	Hübl
0·990	"	Husemann-Hilger	...	...	84	Wiesner			80-84	Allen
0·8500	90	Allen	80·81	Stürcke	83-83·5	Stürcke	3·4	Henriques	78·4	Henriques[4]
0·8422	98 (water 15·5=1)	"	86·87	Schaedler	85-86·1		7·0	"	83·4	"
					90-91·2	Schaedler[3]	0·3-0·5	Berg	79·68	Lewkowitsch
					84	Radcliffe	1·97	Lewkowitsch	80·38	
							2·9	Radcliffe	88·3	Radcliffe

Physical and Chemical Characteristics of Carnaúba Wax—continued

Iodine Value.		Alcohols+Hydrocarbons.[5]		Fatty Acids.[6]		Refractive Index.		
						Butyro-refractometer. "Degrees."		
Per cent.	Observer.	Per cent.	Observer.	Per cent.	Observer.	At 80° C. Calculated to 40° C.	Observer.	
13·5	Lewkowitsch	54·87	Allen and Thomson	47·95	Lewkowitsch	65·7-69	Berg	
·13·2	Radcliffe	55	Stürcke					

[1] Recently purified.   [2] Old specimen.   [3] *Journ. Soc. Chem. Ind.*, 1906, 158.
[4] By saponification in the cold.   [5] Specific gravity of the alcohols at 100° (water at 100°=1) 0·8426 (Archbutt).
[6] Melting point of fatty acids 85° C. (Lewkowitsch).

Lewkowitsch [1] found the acetyl value of carnaüba wax to be 55·24.

When saponifying carnaüba wax strong alcoholic potash must be employed, and the solution must be boiled over a flame for about an hour. If more than 3-4 per cent of water are present in the alcoholic potash, soap is apt to separate which envelops unsaponified wax so that low saponification values are found. The discrepancies in the saponification numbers recorded in the table (p. 877) may thus find their explanation. If strongest alcohol is used, an amyl-alcohol solution (cp. also p. 904) of caustic potash need not be employed, nor is it necessary to boil for twenty-four hours. [2]

Wittels and Welwart examined two samples of carnaüba wax, one pure and one undoubtedly adulterated. They determined the following characteristics :—

	I.	II.
Acid value	5·1	3·9
Saponification value . . .	83·4	62·1
Iodine value	9·0	6·9
Acetyl value	54·8	41·0
Melting point	83° C.	81° C.

These observers conclude from the microscopical examination that the adulterated sample II. is paraffin wax, and calculated its proportion from the saponification value as 26 per cent.

Leys found on examining carnaüba wax by his method (cp. Vol. I. p. 602) the following characteristics :—

Density at 15° C.	0·978
Acid value	7·8
Saponification value	87·0
Ratio number	10·1
Iodine value	9·9
Total saturated acids	47·10 per cent
Melting point of these acids (capillary tube) . .	75° C.
Neutralisation value	78·5
Alcohols	49·22 per cent
Melting point of these alcohols (capillary tube) .	81° C.
Acetyl value	122·0
Hydrocarbons	Nil

Engler [3] found that a 5 per cent solution of carnaüba wax in chloroform gave a deviation of 0·1° to the right in a saccharimeter in a 200 mm. tube.

Valenta [4] examined the melting points of the following mixtures of carnaüba wax with stearic acid, ceresin, and paraffin wax :—

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[1] *Analyst*, 1899, 321.
[2] Cp. Berg, *Chem. Zeit.*, 1909, 886, who recommends to saponify in a solution of xylene (cp. Henriques' method, Vol. 1. p. 106).
[3] *Chem. Zeit.*, 1906, 711.   [4] *Zeitschr. f. anal. Chem.* 23, 257.

Proportion of Carnaüba Wax. Melting Point 85° C.	Melting Point of Mixtures of Carnaüba Wax with		
	"Stearic Acid" of Melting Point 58·5° C.	Ceresin of Melting Point 72·7° C.	Paraffin Wax of Melting Point 60·5° C.
Per cent.	° C.	° C.	° C.
5	69·75	79·10	78·90
10	73·75	80·56	79·20
15	74·55	81·60	81·10
20	75·20	82·53	81·50
25	75·80	82·95	81·70

The table shows that the addition of 5 per cent of carnaüba wax to the substances named produces a considerable increase in their melting point; further additions, however, do not cause a proportional increase.

Stearic acid if present in a specimen of commercial carnaüba wax would be detected by the high acid value of the sample; ceresin and paraffin wax by the high percentage of unsaponifiable matter.

Carnaüba wax is employed in the manufacture of candles, polishing pastes, wax varnishes [1] (waxing coloured papers [2]), phonograph and gramophone records, cable coverings, water-proofing, cerates in pharmaceutical practice, tailors' chalk, etc. It has the property in a greater degree than all other waxes of imparting a lustre to the polishes and preparations made from it.

CANDELILLA WAX

French—*Cire de candélilla*.   German—*Candelillawachs*.
Italian—*Cera di candelilla*.

This wax is obtained from a weed, *Pedilanthus pavonis*, belonging to the *Euphorbiacea*, which grows in the semi-arid regions of Northern Mexico and Southern Texas. The plant attains a height of from 3 to 5 feet, and consists of a bundle of stalks about half an inch in diameter without leaves, and growing on one root. Each plant yields from 3½ to 5 per cent of wax. Another variety, *Euphorbia antisyphilitica*, Zucc., also belonging to the *Euphorbiacea*, yields a similar wax.

These waxes, which form a coating on the entire surface of the plant, are usually obtained by boiling out the shrub with water or steam,[3] but in some cases extraction with benzine is resorted to.[4] The wax prepared by the first process is of a brownish colour which can be bleached by exposure to the sun in thin sheets. The wax is very hard

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[1] *Journ. Soc. Chem. Ind.*, 1894, 744.
[2] A. Wolberg (German patent 93,489) claims wool wax as a substitute for carnaüba wax for this purpose.
[3] Watson, United States patents 1,042,992, 1,058,648.
[4] Sharp, United States patent 1,018,589.

and can easily be powdered, its surface is capable of taking a high polish, and it is said to possess the property of adding lustre to polishes, simulating in this respect, although not to the same extent, carnaüba wax.

Candelilla wax is easily soluble in turpentine, hot chloroform, or carbon tetrachloride. The author suggests the use of the last-named solvent for dissolving the wax on a laboratory scale in order to filter off impurities.

Fraps and Rather [1] isolated, from candelilla wax, a hydrocarbon melting at 68° C. and having the formula $C_{30}H_{62}$, which they state to be hentriacontane, and also another substance, probably a hydrocarbon melting at 85° C. *Sanders* [2] states that the wax contains hentriacontane and myricyl alcohol. This statement is in some measure confirmed by *Lewkowitsch*, [3] who finds that the unsaponifiable matter shows a definite increase on acetylation, namely 4·55 per cent, in contradistinction to *Hare and Bjerregaard*, [4] who state that no increase takes place.

Meyer and Soyka [5] show that the wax, after removal of the alcohol-soluble resinous matter, consisted largely of normal dotriacontane $C_{32}H_{66}$ which melted at 71° C., and also a small amount of an oxylactone $C_{30}H_{58}O_3$ (melting point 88° C.).

Owing to the primitive methods employed in the production of this wax, and also perhaps to other wax-bearing shrubs being mixed with the candelilla plant in gathering it, it is to be expected that the constituents and characteristics will differ very greatly for the various samples.

Candelilla wax should find an outlet in the manufacture of shoe polishes, phonograph records, lacquers, etc. As it is said to burn with a clear bright flame it may, perhaps, be used as a candle material in hot countries.

A sample of the wax from Esparto grass examined by *Lewkowitsch* [3] had the melting point 77-81° C., and contained 56·1 per cent of unsaponifiable matter and 38·6 per cent of fatty acids of the mean molecular weight 468·8. The sample examined contained 4·7 per cent of ash, chiefly silica and alumina. Patents for the recovery of this wax have been taken out by *Cross and Russell*. [6]

[1] *Journ. Ind. and Eng. Chem.*, 1910, 454.
[2] *Proc. Chem. Soc.* vol. xxvii. 250.
[3] Unpublished observation.
[4] *Journ. Ind. and Eng. Chem.*, 1910, 203.
[5] *Monatsh. f. Chem.*, 1913, 1159.
[6] English patent 8268, 1908 ; French patent 395,250.

Physical and Chemical Characteristics of Candelilla Wax

Source.	Specific Gravity at 15° C.	Melting Point.	Solidifying Point.	Acid Value.	Saponification Value.	Iodine Value.	Unsaponifiable Matter. Per cent.	Fatty Acids. Per cent.	Refractive Index at 71·5° C.	Observer.
	0·9930 [1]	68·4	63·8	21·13	54·95	...	...	...	...	Niederstadt
	0·9360 [2]	...	...	19·16	55·23	...	...	...	...	„
	0·950–0·990	68·70	66·68	13·18	50–60	15·20	65·75	...	...	Lüdecke
	...	66	...	19·0	59·7	14·0	...	...	...	Deiler
	0·9850	67·5	...	14·39	46·76	16·6	77·0	...	...	Sanders
Euphorbia antisyphilitica	0·9825	67·68	64·5	12·4	64·9	36·8 [3]	91·2	6·57	1·4555	Hare and Bjerregaard
„	0·9697	65·3	...	10·37	62·93 [4]	35·06	73·48	28·96	„	Lewkowitsch

[1] Brown quality.   [2] Light quality.   [3] By Hanus' method.   [4] Determined with sodium alcoholate.

FLAX WAX [1]

French—*Cire de lin*. German—*Flachswachs*. Italian—*Cera di lino*.

The surface of the flax fibre is coated with a waxy substance which can be isolated by extraction with volatile solvents.

The flax wax so obtained is a white or yellowish-green or yellowish-brown solid substance of dull, wax-like fracture and possesses a very pronounced odour of flax. The wax dissolves with difficulty in chloroform, but is readily soluble in the usual solvents. In alcohol it is only partially soluble.

The fatty acids in flax wax consist of the saturated acids : palmitic and stearic, and of the liquid acids : oleic, linolic, and linolenic. The identity of the liquid acids was proved by the isolation of their oxidation products. The 81·3 per cent of alcohols *plus* hydrocarbons given in the table consist in the main (to the extent of 70-80 per cent) of a solid hydrocarbon, melting at 68° C., and having the specific gravity 0·9941 at 10° C. The remainder is a mixture of phytosterol and ceryl alcohol.

Physical and Chemical Characteristics of Flax Wax [2]

Specific Gravity at 15° C.	Melting Point. °C.	Acid Value.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Reichert-Meissl Value. c.c. $\frac{1}{10}$ norm. KOH.	Alcohols+ Hydrocarbons. Per cent.
0·9083	61·5	54·49	101·51	9·61	9·27	81·32

RAPHIA WAX

This wax, which is obtained from *Raphia Ruffia*, a palm indigenous to Madagascar, forms a whitish layer on the under side of the leaf, from which it can be easily detached by rubbing lightly with the finger. The glossy epidermis of the leaves yields the commercial " bass," and after stripping this off the " residues " are spread on cloths in the open air (but sheltered from the wind). The dried leaves are then shaken or rubbed between the hands, when the wax comes off easily as a fine powder. By boiling with water, the powder is refined ; the earthy matter settles out and the crude wax is ladled off and allowed to solidify.

At present only small quantities are prepared in Madagascar for the market ; but should the demand increase, considerable quantities can be obtained, as the dried leaves, after having been stripped off the " bass," yield about 10 per cent of wax. The crude wax resembles carnaüba wax.

Its specific gravity is 0·950 and its melting point 82° C. (*Jumelle*).[3]

[1] Cross and Bevan, *Journ. Chem. Soc.*, 1890, 196.
[2] C. Hofmeister, *Berichte*, 1903, 1047.
[3] *Compt. rend.*, 1905 (141), 1251.

The wax is sparingly soluble in chloroform, ether, petroleum ether, benzene, carbon-bisulphide, and acetone.. It dissolves in boiling alcohol, but separates on cooling. According to *Haller*,[1] this wax consists chiefly of an alcohol of the formula, $C_{20}H_{42}O$, which is not identical with arachyl alcohol prepared from arachidic acid.

Two specimens of *Raphia* examined in the *Imperial Institute*[2] gave the following result :—

	I.	II.
Specific gravity at 99° C. (water at 15·5° C.)	0·836	0·832
Melting point	82° C.	83° C.
Acid value	4·9	6·5
Saponification value	51·3	50·3
Iodine value	7·7	10·7

COTTON SEED WAX

French—*Cire de coton.* German—*Baumwollsamenwachs.*
Italian—*Cera di cotone.*

This wax is contained in the raw cotton to the extent of about 0·5 per cent, and may be extracted therefrom with benzol. The crude wax resembles beeswax in consistency. *Knecht and Allen*[3] separated the crude wax into two portions by means of petroleum ether; the soluble portion constituting about 70 per cent of the crude wax, melting at 66-67° C. and containing a small amount of combined glycerine, and the insoluble portion which was dark green in colour and plastic, melting at 68° C. These observers separated the petroleum ether soluble portion into two fractions by boiling with 96 per cent alcohol : the alcohol-insoluble portion (18·8 per cent) representing a glossy wax melting at 78° C. and having the iodine value 11·28, and the alcohol-soluble portion melting at 62° C. and having the iodine value 33·42.

The wax contained 47·5 per cent of unsaponifiable matter, from which the authors isolated a phytosterol, the acetate of which melted at 127·2° C. *Piest*[4] extracted from raw American cotton a waxy body by means of the following solvents; the different solvents extracted various amounts, namely :—ether, 0·74 per cent; benzene, 0·87 per cent; petroleum ether, 0·5 per cent; and absolute alcohol, 1·23 per cent. The alcoholic extract had the saponification value 159 and the iodine value 22·1.

[1] *Compt. rend.*, 1907 (144), 594.
[2] *Bull. Imp. Inst.*, 1908, 383.
[3] *Journ. Soc.*, Dyers and Colourists, 1911, 142.
[4] *Zeitschr. f. angew. Chem.*, 1912, 396.

GONDANG WAX [1] (GETAH WAX ?)

French—*Cire de gondang (Cire de getah ?)*.' German—*Gondangwachs (Getahwachs)*. Italian—*Cera di gondang (di getah)*.

This wax is obtained by the Javanese from a wild fig-tree, gondang (*Ficus ceriflua*, Jungh ; *Ficus subracemosa*, Bl.), by boiling the latex with water until the wax separates. The cakes of gondang wax have a chocolate colour outside, and are yellowish-white inside. The yellowish-white colour becomes gradually brown on exposure to the air. The wax is hard and shows conchoïdal fracture, but is not very friable. The crude wax is stated to form a "transition product" between india-rubber and wax. ' The crude wax melts at about 60° C. ; it then forms an extremely viscous mass which can be drawn out in threads, and separates on standing into two layers—melted wax and a brown aqueous layer. On cooling, the wax remains viscous for some time ; finally a white mass separates.

The specific gravity of the melted wax is 1·0115 at 15° C. ; it softens at 55° C., but is not completely melted at 73° C. It dissolves in benzene, carbon bisulphide, chloroform, oil of turpentine, petroleum ether, as also in boiling ether, alcohol, and amyl alcohol. By purifying it with boiling alcohol, 70 per cent of the material are obtained as a white crystalline mass, melting at 61° C., soluble in boiling alcohol and insoluble in cold alcohol.

The purified wax of the melting point 61° C. consists chiefly of the ficoceryl ficocerylate.

On subjecting gondang wax to destructive distillation, an aqueous distillate containing acetic acid and propionic acid is obtained first, followed by an oily liquid containing a hydrocarbon, $C_{14}H_{26}$, a crystalline acid, melting at 54° C., of the formula $C_{12}H_{24}O_2$, and an alcohol, melting at 51° C., of the formula $C_{44}H_{88}O$.

PISANG WAX [2]

French—*Cire de Pisang.* German—*Pisangwachs, Bananenwachs.* Italian—*Cera di Pisang.*

Pisang wax is found as a powdery mass on the leaves of *Cera Musæ*, indigenous to Java. The natives collect the wax in much the same manner as carnaüba wax is gathered, by scraping it off the leaves and melting the scrapings in boiling water. One branch, carrying about seven leaves (each on an average about 6 feet long), yields 60 grms. of wax. The exported wax forms hard cakes of white, yellowish, or slightly green colour. The wax is slightly transparent, of granular

[1] Greshoff and Sack, *Rec. des trav. chim. des Pays-Bas*, 1901, 65. .
[2] *Ibid.*

crystalline fracture, and easily friable. The commercial product contains only 1 per cent of ash.

The specific gravity varies from 0·963 to 0·970; the melting point is from 78° to 81° C., and the saponification value 109.

The wax dissolves sparingly in strong boiling alcohol; it is also sparingly soluble in most solvents. It dissolves easily, however, in boiling oil of turpentine, amyl alcohol, and carbon bisulphide. At 15° C. the following quantities are retained in solution : by petroleum ether 0·1 per cent, acetone 0·5 per cent, ether 0·7 per cent, oil of turpentine 1 per cent, chloroform 1·7 per cent, and carbon bisulphide 1·8 per cent.

The wax consists of the pisangceryl ester of pisangcerylic acid. The commercial samples contain only 1 to 1·5 per cent of free fatty acids.

On subjecting the wax to destructive distillation a small quantity of aqueous distillate passes over whilst the temperature rises rapidly to 200° C. From 210° to 320° C. a buttery mass distils over, which can be separated by expression into a liquid and a solid portion. The liquid portion, after purification by sulphuric acid and re-distillation, appears to be a hydrocarbon having the formula $C_{16}H_{34}$. The solid mass after being crystallised from alcohol melts at 63·5° C., and is stated to have the composition expressed by the formula $C_{27}H_{54}O_2$.

PALM WAX

French—*Cire de palmier.*   German—*Palmwachs.*
Italian—*Cera di palma.*

This wax is obtained from *Ceroxylon andicola*, Humb. (indigenous to the Andes), and *Klopstockia cerifera*, Karst. (indigenous to Columbia). These two palms exude from their trunks a wax-like mass which is collected by the natives. It is a greenish-white powder and is purified in a somewhat crude fashion by melting over fire and boiling with water. This crude product is stated to be a mixture of pure wax with a resinous substance, which can be removed by repeated crystallisation from boiling alcohol, in which the resinous matter is readily soluble. The chemical characteristics are said to be very similar to those of carnaüba wax. It should, however, be noted that commercial products sold as palm wax have frequently been found to be nothing else but carnaüba wax.

Madagascar Rhimba wax is furnished by the "Rhimba" tree of Madagascar. It appeared in commerce a few years ago in the shape of small irregular masses adhering to pieces of bark from the tree. Most of these masses were encrusted with woody and earthy particles, others had a smooth but dull and greyish surface resembling resins, which

harden when running out from the trunks of the trees. Rhimba wax appears, therefore, to consist of a mixture of a vegetable wax and resin.

Jasmine flower wax is obtained from the petals of the jasmine flower, *Philadelphus coronarius*, as a by-product in the process of extracting the flowers with petroleum ether. After evaporating off the petroleum ether, the ethereal oil is extracted from the residue by alcohol, leaving behind a hard yellowish-brown mass for which *Radcliffe and Allan* [1] found the following characteristics :—

Wax—

Acid value	2·8
Saponification value . . .	65·8
Iodine value	52·0

Fatty Acids—

Melting point	57-65° C.
Mean molecular weight . .	398
Iodine value	39

Curcas wax occurring on the bark of *Jatropha Curcas* (see p. 231) consists, according to *Sack*,[2] of melissyl alcohol and melissyl melissate.

Lesser known vegetable waxes are the wax from *Ficus rubiginosa* (*Warren de la Rue and Müller*), the wax from *Antiaris toxicaria*, Lesch. (Upas-tree), ocotilla wax, coffee berry wax [3] (cp. p. 371), the wax from *Langadorffis hypogœa*, Mart. (Balanophore wax), and shellac wax.[4]

Ocotilla wax [5] is obtained from a shrub *Moquinia hypolenca*, D.C. (*Fouquiera splendens*), belonging to the order *Compositœ*, growing wild on the coast of Rio Grande. The author obtained a yield of about 2 per cent from the entire plant, the bulk of which, however, was contained in the leaves, the stem and the stalks yielding but a small proportion. The extracted wax had the following characteristics :—

Acid value . . .	58·1
Saponification value . . .	⌐ 185·0 (?)
Unsaponifiable matter . .	43·11 per cent
Melting point of same . .	64-66° C.
Fatty acids	23·9 per cent
Melting point of same . .	60° C.
Mean molecular weight . .	268·3

[1] *Journ. Soc. Chem. Ind.*, 1909, 227.
[2] *Chem. Centralbl.*, 1906, i. 1106.
[3] Meyer and Eckert, *Monatsh. f. Chem.*, 1910, 1250.
[4] Ljubarski, *Seifensiederztg.*, 1913, 127.
[5] Cp. F. Ephraim, German patent 216,792.

• CANE SUGAR WAX

French—*Cire de sucre de cane.*   German—*Rohrzuckerwachs.*
Italian—*Cera di zucchero vegetale.*

This wax is obtained as a by-product in the manufacture of sugar from the cane either by scraping the stem or skimming off the juice obtained by boiling out the cane. *Wijnberg* has patented a process for recovering the wax from the filter press residues obtained in the purification of the sugar juice with lime.[1]   In the factories the residues from the filter presses are allowed to ferment when the glycerides appear to be decomposed, the more resistant wax-like bodies remaining unattacked. *Wijnberg* examined the samples of the crude wax prepared from both the fresh and fermented residues, and obtained results collated in the table of characteristics. *Wijnberg*[2] also found a large amount of lecithin and a phytosterol.

The crude wax is a dark brown or dark green, hard mass, and some specimens are sticky to the touch.

[1] United States patent 941,401 ; French patent 397,843 ; English patent 1322, 1909.
[2] *Inaug. Dissert.*, Amsterdam, 1909.

Physical and Chemical Characteristics of Cane Sugar Wax

	Specific Gravity at 100/15.	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.	Acid Value.	Reichert-Meissl Value.	Insoluble Acids + Unsaponifiable. Per cent.	Unsaponifiable Matter.	Fatty Acids.	Glycerol.	Acetyl Value.	Observer.
Fresh wax	0·968	51	55~	167·9	60	38·6	7	88·66	27·7	..	7·2	..	Wijnberg
Decomposed wax	0·981	..	55-79	45·5-57	13·4-16·2	8·4-12	..	..	55·80	..	..	55·60	"
	0·8785	..	58-59	81·1	87·7	11·9	..	..	69·1	33·28	..	..	Lewkowitsch

. 2. ANIMAL WAXES

The animal waxes contain but small quantities of unsaturated acids and unsaturated alcohols. The acid and alcoholic constituents of beeswax, spermaceti, and insect wax belong chiefly to the saturated (aliphatic) series. Wool wax, however, has an exceptional chemical composition; some of its alcohols are derivatives of the cholesterol series, and its fatty acids are characterised by the facility with which they become dehydrated. Wool wax is also remarkable on account of the difficulty with which it is saponified even by alcoholic caustic potash.

Like all natural products the individual waxes exhibit variations depending on the race of the animal, etc. This holds especially good of the different beeswaxes.

WOOL WAX [1] (WOOL GREASE)

French—*Cire de suint.* German—*Wollwachs.* Italian—*Cera di lana.*

For tables of characteristics see pp. 891, 892.

The term *wool wax* was proposed by the author for the neutral portion of raw wool fat—" wool grease,"—and has now been adopted by modern writers.

Wool fat, Wool grease, Recovered grease, Brown grease : [2] French— *Suintine* ; German—*Wollfett, Wollschweissfett, Suinter* ; Italian—*Grasso di lana greggio, sugna,* is the natural grease contained in sheep's wool. In the course of preparing the raw wool for spinning, this grease is removed by means of dilute soap (or sodium carbonate) solutions,[3] or by extraction with volatile solvents. In this country the suds from wool-scouring are usually collected in large tanks, and by acidulating with mineral acids, "brown grease," or "recovered grease," [2] is obtained of varying composition, according as to whether the suds from the wool are kept separate or are mixed with the soap suds from the scoured woven goods, which latter process is the one adopted in those woollen mills where wool is washed, spun, and woven (cp. Vol. III. Chap. XVI. "Wool Grease"). The degreasing of wool by means of an electric current has been patented by *Lagye and Vandatte.*[4]

The wool grease, obtained by extracting raw wool with volatile solvents, contains of course only the natural constituents, viz. free fatty acids, neutral esters, and free alcohols, in admixture with potassium salts of fatty acids.

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.,* 1892, 135 ; 1896, 14.
[2] In the United States this grease is known commercially as "Dégras."
[3] Dantzer (French patent 372,757) patents the employment of aqueous solutions containing only the water-soluble portions of wool-scouring suds.
[4] French patent 399,875.

The wool fats from various sources vary considerably within certain limits much as other natural products do. The following table contains some characteristics of several wool fats obtained by extracting raw wool with ether :—

Source of Wool Fat. From	Yield of Wool Fat. Per cent.	Potash Salts in Wool Fat, calculated to Potaseium Oleate. Per cent.	Colour.	Con- sletence.	Acid Value.	Saponifica- tion Value.	Alcohole (unsaponi- fiable). Per cent.	Ob- server
1. New Zealand wool	16·6	4·9	dark red	fairly eoft when fresh, becomes harder on keeping.	14·3	110·5-110·7	43·6-43·9	Herbt
2. Australian wool	16·0	4·24	brownish- yellow	fairly soft, re- mained so after keeping.	15·5	112·7-113·3	..	,,
3. South American wool	13·2	9·25	yellowish- olive-green	fairly hard.	13·2	98·7-98·9	43·1-43·6	,,
4. Russian wool	6·6	24·4	dirty brown	soft at 20° C.	18·0	94·2-95·9	38·7-39·1	,,
5. Australian wool			light brown	melts at 30 6° C.	27·4	100·8	55·124	Lewko witsch

Since the valuable property of wool fat, viz. that of yielding emulsions with water which are easily absorbed by the skin, has been re-discovered,[1] the raw wool fat is purified by various (patented[2]) processes, and the refined neutral wool fat—*wool wax*—is brought into commerce either in an anhydrous state (under such names as " adeps lanæ "), or in the hydrated state (under the name " lanolin "). Other commercial names are " agnin," " alapurin," etc. (cp. Vol. III. Chap. XVI." Wool Grease ").

Anhydrous wool wax is a pale yellow, translucent substance, having a slight but not unpleasant smell (in contradistinction to raw wool grease, which is characterised by its peculiar disagreeable smell, recalling that of sheep). Its consistence is that of a thin ointment. It dissolves readily in chloroform, ether, and ethyl acetate. Although insoluble in water, it possesses the remarkable property of absorbing larger quantities of water than any other wax ; even if as much as 80 parts of water be mixed with 100 parts of wax, the emulsion which is formed with water has the appearance of a perfectly homogeneous mass. A mixture of neutral wax and water, containing about 22-25 per cent of the latter, is sold in commerce under the name " lanolin " (see below).

Wool wax is not completely saponified by aqueous caustic alkalis ; even prolonged boiling with alcoholic potash under ordinary pressure does not effect complete saponification. Sodium alcoholate (or absolute alcohol and metallic sodium) or alcoholic potash under pressure readily effect complete saponification (cp. Vol. I. Chap. II.).

[1] *Journ. Soc. Chem. Ind.,* 1892, 136 ; 1896, 14.
[2] Cp. Langbeck, *Journ. Soc. Chem. Ind.,* 1890, 356.

I. Physical and Chemical Characteristics of Wool Wax (i.e. Esters and Free Alcohols)

Specific Gravity			Solidifying Point		Melting Point		Saponification Value		Iodine Value	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
17	0·9449[1]	Rosauer	30-30·2[2]	Lewkowitsch	39-42·5	Stockhardt	102·4[2]	Lewkowitsch	25·9-26·8[2]	Lewkowitsch
17	0·9413[3]	,, Allen			36-41	Benedikt			25·8-28·9[2]	,,
98·5 (water 15·5=1)	0·9017				31-35 }[2] 39-41 }	Lewko- witsch			17·1-17·6[4]	,,

I. Physical and Chemical Characteristics of Wool Wax (i.e. Esters and Free Alcohols)—continued

Fatty Acids.		Alcohols.		Refractive Index.	
Per cent.	Observer.	Per cent.	Observer.	At 40° C.	Observer.
59·8	Lewkowitsch	43·6	Lewkowitsc'	1·4781- 1·4822	Utz
		51·8[4]	,,		

[1] From anhydrous lanolin.　[2] From raw wool fat.　[3] From "Adeps lanæ," Chem. Centralbl., 1898, ii. 875.　[4] Prepared from "lanolin."

II. *Physical and Chemical Characteristics of the Insoluble Fatty Acids*

Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Iodine Value. Per cent.	Observer.
40	41·8	327·5	17	Lewkowitsch

III. *Physical and Chemical Characteristics of the Mixed Alcohols*

Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Iodine Value.	Acetyl Value.	Observer.
28 [1]	33·5 [1] 44·4-48·9 [2]	239 [1] ...	36 [1] 26·4 [2]	... 143·8 [2]	Lewkowitsch ,,

IV. *Chemical Characteristics of the Neutral Esters*

Saponification Value.	Fatty Acids.	Alcohols.	Observer.
Mgrms. KOH.	Per cent.	Per cent.	
96·9	56·66	47·55	Lewkowitsch

The chemical composition of wool wax is not fully known. Wool wax evidently consists of a very complex mixture of esters and free alcohols; amongst the alcohols, cholesterol and isocholesterol occur to a large extent. Owing to the presence of high proportions of these alcohols wool wax rotates the plane of polarised light. *Walden* found the specific rotation $[a]_D = +6.7°$ at 35° C., and in a 25 per cent chloroform solution $[a]_D = +8.55°$. In a 25 per cent benzene solution *Rakusin* found $[a]_D = +12.8$.

Lewkowitsch was the first to show that the previously accepted statement, viz. that neutral wool wax is a mixture of cholesteryl (and isocholesteryl), oleates, and stearates, is erroneous. The low iodine value of both the fatty acids and the alcohols precludes this altogether. The absence of palmitic and stearic acids has been confirmed later on by *Darmstädter and Lifschütz*,[3] Nor should *Buisine's* assertion that ceryl ceretate[4] is present be accepted without further proof, as ceryl alcohol occurs in raw wool fat in the free state. An inquiry into the nature of

[1] From raw wool fat. 　　[2] From lanolin. 　　[3] *Berichte*, 1898, 103.

[4] G. de Sanctis, *Chem. Zeit.*, 1895, 651, states that cerotic acid occurs in wool fat. According to Darmstadter and Lifschutz, the quantity of cerotic acid can only be very small.

the components, carried out by the author,[1] has shown that the mean molecular weight of the alcohols (239), in conjunction with the low iodine value (36), points to the presence of lower saturated alcohols, since cholesterol and isocholesterol have the molecular weight 372 and the iodine absorption 68·3 (cp. Vol. I. Chap. II.). The fatty acids, owing to their low iodine absorption, cannot consist to any considerable extent of oleic acid. The author has shown that they contain hydroxy acids,[2] as they easily give off the elements of water at temperatures little above 100° C., with formation of inner anhydrides or lactones, and assimilate considerable quantities of acetic anhydride, forming acetylated acids.

Marchetti [3] stated that he isolated from wool wax an alcohol of the formula $C_{12}H_{24}O$—termed lanolin alcohol. Since, however, two other alcohols described by *Darmstädter and Lifschütz*,[4] and supposed to form a homologous series with lanolin alcohol, have been shown to be lactones (see above), the existence of this alcohol becomes doubtful.

The results of a further examination of wool wax carried out by *Darmstädter and Lifschütz* [5] have been collated by the author in a synoptical form in the following table [6] :—

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[1] *Journ. Soc. Chem. Ind.*, 1892, 136 ; 1896, 14. Cp. Vol. I. Chap. XI.
[2] *Ibid.*   [3] *Gazz. chim. ital.*, 1895, 22.
[4] *Berichte*, 1895, 3133 ; cp. *Jahrbuch d. Chem.*, 1896, vi. 375.
[5] *Ibid.*, 1896, 618 ; 2890 ; *Journ. Soc. Chem. Ind.*, 1896, 548 ; 1897, 150.
[6] *Jahrbuch d. Chem.*, 1898, viii. 405.

Wool Wax[1] *separated by Amyl Alcohol into two Parts : A and B*

A. Hard Portion,[1] forming about 10 to 15 per cent of the Wool Wax. Resolved into		B. Soft Portion, forming about 85 to 90 per cent of the Wool Wax. Resolved into			
(α) Acids, about 60 per cent.	(β) Alcohols, containing	(α) Acids, about 40 to 50 per cent, containing	(β) Alcohols; about 55 to 60 per cent resolved by means of Methyl Alcohol into two Fractions.		
			1st Fraction resolved into Two Groups.		2nd Fraction, containing
			1st Group.	2nd Group.	
(1) Lanoceric acid	(1) Ceryl alcohol	(1) A liquid acid (about 40 per cent)	Containing ceryl alcohol, carnaubyl alcohol	Containing small amounts of ceryl and carnaubyl alcohols, and chiefly isocholesterol (11 per cent), differing from *Schulze's* isocholesterol as regards crystalline form, solubility, and composition, but identical with it as regards melting point and chemical reactions	Alcohol 2 *a* (3-4 per cent of B)
(2) Lanopalmic acid	(2) Carnaubyl alcohol[2]	(2) Myristic acid			Alcohol 2 *b* (6-7 per cent of B)
(3) Myristic acid	(3) Cholesterol	(3) Carnaubic acid			Alcohol 2 *c*[3] (50-54 per cent of B)
(4) Carnaubic acid	*Isocholesterol* is absent	Neither lanoceric nor lanopalmic acids were present			
(5) A liquid acid					
(6) A volatile acid					

[1] Darmstädter and Lifschutz term the hard fat A "Wool wax," but for chemical reasons the name wool wax should embrace all the neutral portions contained in wool wax.

[2] The existence of this alcohol must be doubted since Mathes and Sander (*Arch. d. Pharm.*, 1907 (246), 169) have shown in the preparation of melissyl alcohol from the unsaponifiable matter of laurel oil that a substance was obtained which simulated completely the carnaubyl alcohol described by Darmstädter and Lifschutz, but was found on further examination to be a mixture of a hydrocarbon, melting at 69° C.. and of pure melissyl alcohol.

[3] This portion appears to contain the bulk of the water-emulsifying substances in wool fat (Lifschutz, German patent 171,178; cp. also Vol. III. Chap. XVI.). According to Lifschutz (*Monatsh. f. prakt. Dermatol.*, 1907, 235), this fraction would appear to contain oxycholesterol $C_{26}H_{44}O_2$, oxycholesterol ester $(C_{26}H_{43}O)_2O$, and other hitherto not identified derivatives of cholesterol.

The alcohols mentioned under B (β) do not contain cholesterol. The alcohol " 2 c " gives the colour reactions of cholesterol, but since cholesterol itself could not be isolated, *Darmstädter and Lifschütz* concluded that cholesterol is only formed during the reaction, and that the alcohol " 2 c " should be looked upon as a hydrated cholesterol, from which cholesterol and isocholesterol are obtained. Further researches are required to elucidate the complicated composition of wool wax. Since cholesterol and isocholesterol differ in their optical rotation (cholesterol being lævorotatory and isocholesterol dextrorotatory in ethereal solution), the polariscopic examination of the alcohols should lead to more definite information (Vol. I. Chap. I.). This is all the more required since in a more recent publication *Schulze* [1] maintains his earlier statements on isocholesterol.

A renewed inquiry into the work of *Darmstädter and Lifschütz* by *Röhman and Siebert* [2] has, however, proved that part of the substances which had been obtained by *Darmstädter and Lifschütz* are only formed in the course of, and are due to the manner of, preparing the products described by them, and that another part does not consist of chemical individuals, but of a mixture of the original substances with their products of saponification. As far as can be stated at present wool wax contains *lanocerin*, which is isolated by repeatedly boiling out wool fat with an equal amount of methyl alcohol, dissolving the undissolved portion in ether, and precipitating it with alcohol. Lanocerin appears to be the inner anhydride of lanoceric acid. With regard to carnaübyl alcohol see footnote, p. 894, and Vol. I. Chap. III.

To some extent the differences in the results obtained by the several observers may be due to the difference in the composition of the wool fats from which the wool waxes were isolated.

Lewkowitsch [3] found the acetyl value of a sample of wool wax from " lanolin " 23·3, and of the wool fat alcohols 143·8.

Owing to its property of forming an emulsion with water (which will not separate into two layers even after several years' standing), and to the ease with which it is absorbed by the skin, wool wax is used as a basis for ointments [4] and cosmetics.[5] The British and the German Pharmacopœia recognise two preparations, viz. Adeps lanæ anhydrous, *i.e.* pure wool wax, and Adeps lanæ hydrosus, *i.e.* hydrous wool wax, better known under the trade term " Lanolin."[4] For further information on the subject of wool fat cp. Vol. III. " Wool Grease."

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[1] *Berichte*, 1898, 1200.   [2] *Centralbl. f. Physiol.* 1905, xix. No. 10.
[3] *Analyst*, 1899, 321.
[4] With regard to the solubility of mercuric chloride, mercuric nitrate, sulphur, ferrous sulphate, ferric chloride, lead acetate, iodine, potassium iodide, iodoform, phenol, and camphor in lanoline, cp. G. Close, *Archives internationales de pharmacodynamie et de thérapie*, 1907, 460.
[5] Cp. P. G. Unna, *Medizinische Klinik*, 1907, No. 42.

BEESWAX [1]

French—*Cire d'abeilles*. German—*Bienenwachs*. Italian—*Cera d' api*.

For table of characteristics see p. 920.

Beeswax is secreted by the common bee, *Apis mellifica*, as also by other species of *Apis* and *Trigona*, as a product of digestion; it serves to the bees as the material for building up the honeycombs.

At present the honey is removed from the combs by centrifugal machines. A description of modern apparatus has been given by *W. F. Reid*.[2]

For places of production see table, p. 909.

The older process of preparing beeswax consisted in melting the emptied honeycombs by immersion in hot water, and filtering the liquefied wax from impurities (such as dead bees, etc.).[3] A more modern process is to prepare the wax by expression after having melted the honeycombs and removed gross impurities by straining. The press-residue is again boiled up and pressed once more. The residue from the second expression still contains some 10-15 per cent of wax. Such residues are collected together in special establishments, and the wax is recovered by extraction with solvents.[4] This product, known as "extracted beeswax," differs somewhat from the beeswax obtained by expression. It presents a dark brown, soft mass, greasy to the touch and of unpleasant odour; on boiling with water it gives up a yellow colouring matter. *Hirschel*[5] examined three genuine samples of "extracted" wax. Chemically they differed from expressed wax by having a somewhat higher acid value (23·3-27·1) and a much higher iodine value (31·2-39·6). In *Weinwurm's* paraffin wax- or ceresin-test (see p. 921) they behaved like samples of genuine beeswax containing about 5 per cent of admixed paraffin wax. Since "extracted" beeswax is rarely sold in commerce as such, the following notes refer only to expressed wax, *i.e.* the yellow wax of commerce.

Gabrilowitsch[6] examined samples of Russian extracted wax and found the following characteristics:—

Specific gravity	.	.	.	0·95-0·97
Melting point, °C.	.	.	.	60-64
Acid value	.	.	.	·18-22
Saponification value	.	.	.	88-100
Ratio number	.	.	.	3·55-3·88

The propolis (German "Klebwachs"), *i.e.* the wax used by the

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[1] The bibliography of beeswax arranged chronologically, and of waxes used in adulterating it, will be found *Journ. Soc. Chem. Ind.*, 1892, 756.

[2] *Journ. Soc. of Arts*, 1903, 522.

[3] Cp. *Bull. Imp. Inst.*, 1910, 25.

[4] A. C. Miller, United States patent 905,732.

[5] *Chem. Zeit.*, 1904, 212.   [6] Russ, *Führer d. d. Fettind.*, 1909, 56.

bees for sealing up the cells, consists, according to *Greshoff and Sack*,[1] of 84 per cent of an aromatic resin, 12 per cent of wax, and 4 per cent of alcohol-soluble impurities. A more recent analysis of propolis by *Dieterich* [2] gave the following results :—

Volatile substances	.	.	.	.	5·96 per cent
Alcohol-insoluble substances	.	.	.	12·94	,,
Resinous substances	.	.	.	64·61	,,
Wax	.	.	.	.	16·05	,,
Volatile oils	.	.	.	.	Traces

P. Borisch [3] gives the following data :—Resinous matter insoluble in hot light petroleum spirit, but soluble in 96 per cent alcohol 43·6 per cent ; "Propolis balsam," soluble in hot light petroleum spirit and 70 per cent alcohol 8·7 per cent ; Beeswax 27·9 per cent ; Ethereal oil and Water 6·9 per cent. The "propolis resin" is described as being brownish black, soft, and melting at about 67° C. ; after exposure for several hours to a temperature of 101° C. it assumes on cooling the consistence of hard Tolu balsam. The "propolis balsam" is described as a syrupy, golden yellow fluid, having a strongly aromatic odour.

If the propolis is melted with the beeswax it imparts a more intense colour. For its analysis *Kustenmacher* [4] recommends to boil out the sample 5 times with twice its weight of 99·8 per cent alcohol (by volume). The insoluble portion is subsequently extracted with chloroform, and the final residue weighed. The alcoholic solution on cooling yields a precipitate which is washed with absolute alcohol and finally with 96 per cent alcohol. The washings and filtrate are separated into further fractions by careful dilution of water. *Dieterich* extracted a propolis with low boiling petroleum ether and separated the wax and balsam by means of 70 per cent alcohol. This author states that propolis contains vanillin, but no cinnamic acid.

In order to increase the production of honey it has become the practice to place artificial combs in the beehives. These combs were originally made from genuine beeswax, but with the increased demand for beeswax, artificial combs are now being prepared from a mixture of beeswax and beeswax substitutes. At first ceresin was used for this purpose, but at present paraffin wax has taken its place. When such combs, after the removal of the honey, are melted down, then naturally the resulting wax will contain paraffin wax. Such a product must, of course, be looked upon as adulterated. Latterly stearic acid is being used in place of (or admixed with) paraffin wax (see p. 912).

The expressed wax is as a rule of a yellow or yellowish colour. Some commercial waxes, mostly of non-European origin, have a greenish, reddish, or brown colour, even black if the melting out is done carelessly. Cuban wax in particular varies from light yellow to black. The chief

[1] *Rec. Trav. Chim. des Pays-Bas*, 1903, 139.
[2] *Zeitschr. f. angew. Chem.*, 1907, 1688.
[3] *Pharm. Zentralbl.*, 1907 (48), 929.
[4] *Berichte d. Dent. Pharm. Ges.*, 1911, xxi., 65.

sources of origin of beeswax are given in the tables, pp. 909 to 914. The crude beeswax, like all other natural products, varies not only with the race of the bee and the kind of food it takes, but also with the care exercised in preparing the wax. Thus the wax obtained from bees who frequent pine forests is darker than that obtained from bees who collect the pollen from clover. Light coloured wax is considered of higher value than dark coloured, inasmuch as the former is bleached more readily than the latter. This must, however, not be taken as a general rule, as some dark waxes of foreign origin can be easily bleached.

The crude wax is subjected in wax refining works to a process of purification, followed, if required, by a process of bleaching.

The purification consists in remelting the wax in pitch pine vessels over boiling water so that the impurities (dirt, etc.) may settle out. In order to accelerate the settling process, and with a view to obviating as far as possible the troublesome emulsion which forms between the aqueous and the wax layers, dilute sulphuric acid is frequently added to the water over which the wax is heated. After thorough boiling and agitating, the contents of the vessels are allowed to rest, when clear wax rises to the top and is skimmed off to be poured into moulds. Yellow wax has the pleasant odour of honey, and is almost tasteless. At low temperatures it is brittle, and of fine granular fracture. The observation that yellow wax becomes white by repeated melting in water and by exposure to sunlight has led to the customary process of " air bleaching " or " sun bleaching " yellow wax. It was found by experience that the moisture of the air, the intensity of the light, and especially the extent of the surface that is exposed to the air, play a very important part in the process of bleaching. In order to expose as large a surface as possible, the yellow wax is usually converted into ribbons, or strips, or granules.[1] The wax is also made into flakes by pouring it in its melted state on to rollers which are partly immersed in water. It has also been found by experience that an admixture of 3-5 per cent of tallow or of a small quantity of oil of turpentine is capable of accelerating the process of air bleaching. It would appear that the oil of turpentine acts as an oxygen carrier, inasmuch as it gives rise to the formation of hydrogen peroxide, which is used as a bleaching agent in the production of white wax (see below). (At the same time the oil of turpentine renders the beeswax less friable, cp. Vol. III. " Wax candles.")

Owing to the slowness of the air-bleaching process, other methods are employed, such as decolourising by treatment with animal char, or with fuller's earth ; [2] purely chemical processes of bleaching, viz. by means of hydrogen peroxide, ozone, potassium bichromate and sulphuric acid, and by means of sodium hypochlorite, are also frequently resorted to. With the improvements in the commercial preparation of ozone, it, in the form of ozonised air,[3] has been used for bleaching beeswax.

[1] Perhaps an apparatus like *Laral's* emulsifier may prove useful in comminuting beeswax to granules.

[2] Weingartner, French patent 365,555, 1906 ; A. Muller-Jacobs, United States patent 883,661. A. Lob, *Chem. Revue*, 1908, 81.

[3] Ozonair Ltd., English patent 4579, 1906.

This method possesses several advantages over the purely chemical processes, inasmuch as the bleached wax is harder and the danger of charring is obviated. A large plant for this purpose has recently been fitted up in Russia. Whereas air-bleached wax is suitable for every purpose for which wax is used, chemically bleached waxes, especially those obtained by treatment with potassium bichromate and sulphuric acid, or sodium hypochlorite, are not suitable for best candles. It has therefore become a practice in many establishments to combine the process of chemical bleaching with air bleaching, by first treating the wax with chemicals and then "finishing it off" by exposure to light and air.[1] Chemically bleaching requires as much circumspective attention to details as in the case of oils and fats. If not carefully attended to dark wax results, from which the metallic salts cannot be washed out readily. Especially dangerous is bleaching with free chlorine, although bleaching with sulphuric acid and potassium chlorate has been proposed.

All waxes do not bleach equally well, much as is the case with many individual oils and fats of different origin. Belladi wax is the easiest to bleach ; it is followed in this respect by Turkish wax, Chilian wax, and Smyrna wax. Gambia wax is not bleached satisfactorily by air, but can be bleached by chemicals. Brazilian wax has not hitherto been bleached successfully. Italian waxes are more difficult to bleach. Whereas bleached Belladi wax is white with a blueish tint, other waxes give a yellowish tint, or are of a greenish or greyish hue. The art of the wax-bleacher consists in selecting and blending the various natural products so as to obtain a substance of desired tint, as also of the desired hardness by mixing hard and soft (such as Mogador) waxes.

Best bleached white wax is of a pure white, or slightly yellowish colour. It is odourless and tasteless, has a higher specific gravity than yellow wax, and is more brittle than the latter. It is transparent at the edges ; its fracture is smooth, and no longer granular.

Beeswax is not greasy to the touch, but if dropped on paper in the melted state it causes a permanent transparent spot.

Beeswax found in the grave of a Viking queen at Oseberg in Norway, probably dating from A.D. 800, showed the following characteristics (as recorded by *Sebelien*[2]) :—

Specific gravity at 15° C.	.	.	.	0·962
Melting point, ° C.	.	.	.	63
Acid value	.	.	.	16·6
Saponification value .	.	.	.	95·34
Ratio number	.	.	.	4·74
Iodine value .	.	.	.	66·02

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[1] The bleaching of wax by air was practised by the ancient Greeks and Romans. *Pliny* describes bleached wax as "cera punica." A description of the process of converting beeswax into ribbons and bleaching by exposure to air and light is given by *Dioscorides*.

[2] *Zeitschr. f. angew. Chem.*, 1913, 689.

Beeswax [1] consists chiefly of a mixture of crude *cerotic acid* [2] and *myricin* (melissyl [myricyl] palmitate). It also contains, in small quantities, free melissic acid, $C_{30}H_{60}O_2$ (or $C_{31}H_{62}O_2$), *myricyl dlcohol (Schwalb)*,[3] uncombined *ceryl alcohol*, and another alcohol of unknown composition (perhaps psyllostearyl alcolfol found by *Sundwick* [4] in bumble bees' wax). *Berg* found upwards of 0·6 per cent of cholesterin esters. Small quantities of unsaturated fatty acids have also been isolated. Hydrocarbons also are normal constituents of beeswax. *Schwalb* isolated two hydrocarbons :—*heptacosane*, $C_{27}H_{56}$, melting at 60·5° C., and *hentriacontane*, $C_{31}H_{64}$, melting at 67° C.

With regard to the proportion of hydrocarbons in beeswax the earlier statement made by *Schwalb*, who found 5-6 per cent, is erroneous ; for *A. and P. Buisine* obtained from 12·7 to 13·0 per cent of hydrocarbons. These belong partly to the ethylene series. *Mangold* [5] confirmed *Buisine's* results. *Kebler* found 12·5-14·5 per cent. More recently *Hett and Ahrens* obtained from 12·8 to 17·35 per cent of hydrocarbons (cp. p. 910). The Indian beeswaxes ("Ghedda waxes ") contain on an average only 8·6 per cent of hydrocarbons. The melting points and iodine values of the hydrocarbons contained in pure beeswax are collated in the following table :—

Melting Point	Iodine Value.	Observer.
° C. 49·5	22·05	A. and P. Buisine
51·0	22·5	Mangold
55·2	20·1	Ahrens and Hett

Engler [6] found a 5 per cent chloroform solution of yellow beeswax to rotate the plane of polarised light to the right (10·15° in a 200 mm. tube in a saccharimeter).

Beeswax is almost insoluble in cold alcohol. Boiling alcohol dissolves the bulk of the cerotic acid and a small quantity of myricin The alcoholic solution reddens blue litmus paper faintly ; a solution of phenolphthalein made just pink by a trace of alkali is, however, instantly decolourised. On cooling, the cerotic acid separates out so completely (in the form of thin needles) that the alcoholic solution does not become turbid on adding water, a slight opalescence only being noticeable.

[1] Brodie, *Liebig's Annal.*, 67, 180 ; 71, 144. Schalfejeff, *Berichte*, 1872 (9), 278 ; 1688. Nafzger, *Liebig's Annal.*, 224, 225 ; Schwalb, *ibid.*, 235, 106. Marie, *Journ. Soc. Chem. Ind.*, 1894, 207 ; 1895, 599 ; 1896, 362.
[2] Containing about 30-40 per cent of homologous acids (Marie). The melting point of the isolated and recrystallised "cerotic" acid is given by various observers as 78°-79° C.
[3] According to Gascard (*Journ. Soc. Chem. Ind.*, 1893, 955) the myricyl alcohol from beeswax is identical with that from carnauba wax and has the formula $C_{31}H_{64}O$.
[4] *Zeitschr. f. phys. Chem.*, 1907, **53**, 563.   [5] *Journ. Soc. Chem. Ind.*, 1891, 861.
[6] *Chem. Zeit.*, 1906, 711.

Pure beeswax is soluble in chloroform. The best solvent for beeswax is carbon tetrachloride.

Warm ether dissolves beeswax readily; on cooling, however, a portion of the dissolved wax separates out. According to *Robineaud,*[1] only 50 per cent of beeswax are dissolved by ether at the ordinary temperature. Experiments made by *Buchner*[2] showed that after allowing beeswax to stand with ether at the ordinary temperature, and washing the insoluble portion, a deep yellow ethereal solution was obtained, whereas a white mass remained undissolved. The ether-soluble portion represented 30 per cent, the ether-insoluble portion 70 per cent of the original wax. The following table indicates the difference in composition of the soluble and the insoluble portions :—

	Acid Value I.	Saponification Value. II.	Difference. II.-I.	Ratio Number.
Original beeswax . .	19·5	96·2	76·7	3·93
Ether-soluble portion .	40	83·8	43 8	1·905
Ether-insoluble portion	11·7	99 1	87·5	7·5

From these numbers the conclusion must be drawn that the major portion of cerotic acid, colouring matters, and hydrocarbons, together with the minor portion of the wax esters, pass into the ether. The ether-insoluble substance contains, therefore, a small quantity of cerotic acid and the main portion of the wax esters. Beeswax dissolves in hot benzene, but at 20° C. a considerable portion separates out, even from a 1 per cent solution of beeswax in benzene.

The free cerotic acid cannot be extracted from beeswax by treatment with sodium carbonate or caustic alkali, as the resulting soap solution forms with the beeswax esters a complete emulsion which does not separate, even after many months' standing (similarly as in the case of wool wax).

On distilling beeswax with lime an oil passes over (beeswax oil[3]), the specific gravity of which varies from 0·74 to 0·79. On subjecting beeswax to destructive distillation *Greshoff and Sack*[4] obtained an oily distillate which separated into a solid and a liquid portion. The liquid portion contained a hydrocarbon of the composition $C_{15}H_{30}$. The solid portion still contained undecomposed wax, and gave, after saponification, a solid fatty acid of the melting point 63° C. The unsaponifiable matter contained a hydrocarbon having the composition C_nH_{2n} and melting at 56° C.

Eckecrantz and Lundström[5] resolved the product into (1) hydrocarbons

[1] *Dingl. Polyt. Journ.,* 1862, 60.

[2] *Chem. Zeit.,* 1907, 571.

[3] Ettling, *Liebig's Annal.* (1832), 2, 225 ; Poleck, *Liebig's Annal.,* 1848 (67), 174 : Brodie, *ibid.,* 1849 (71), 144 ; *Journ. Soc. Chem. Ind* 1895. 1050.

[4] *Rec. Trav. Chim. des Pays-Bas,* 1901, 75.

[5] *Arch. d. Pharm.,* 1910 (248), 500.

volatile in a current of steam ; these appear to consist of hydrocarbons ranging from $C_{10}H_{20}$ up to $C_{16}H_{32}$; (2) liquid hydrocarbons, no longer volatilisable in a current of steam, consisting of hydrocarbons ranging from $C_{16}H_{32}$ to $C_{27}H_{54}$; and (3) a solid saturated hydrocarbon of the composition $C_{29}H_{60}$ (*Nonokosane*). The solid hydrocarbon forms the bulk of the wax oil.

Beeswax is very frequently adulterated. *Water* and *mineral matters* (such as ochre, gypsum, etc.), also *flour* and *starch*, are easily detected. Fraudulent admixture with *tallow, Japan wax, stearic acid, paraffin wax* and *ceresin, colophony* (*rosin*), *spermaceti, carnaüba wax, insect wax,* and *wool wax* may be detected by the methods described below.

Previous to the detailed examination by physical and chemical tests, the sample of crude beeswax should be boiled with water (to remove honey) and filtered in a water oven. Gross adulterants, such as mineral matters, are thus easily detected and determined quantitatively. The determination of *water* should not be omitted.

A preliminary test for the detection of adulterants consists in dissolving the sample in chloroform (*Long* [1]). Since ceresin, paraffin wax, carnaüba wax, and wool wax are not completely soluble in this menstruum, considerable quantities of the latter may thus be detected qualitatively. It should, however, be borne in mind, that bleached (white) beeswax is not readily soluble in chloroform (*Dieterich* [2]).

As a preliminary test to which the filtered wax may be submitted, refractometric examination has been recommended by *Prosio, Marpmann, Werder,*[3] and later by *Berg.*[4] Owing to the high melting point of the wax, the refraction should be determined at 75°-80° C. Since the melting point of most beeswaxes lies above 65° C., the numbers recorded in the literature on this subject for a temperature of 62° C. have been omitted in this work, as being open to serious doubts. The figures given in the table have been determined at 84° C., but were reduced by calculation to 40° C. (*Berg*). (The numbers actually observed have not been published.) Considerable quantities of carnaüba wax, colophony, ceresin, paraffin wax, and stearic acid, can be preliminarily detected by the refractometric method, as will be seen from the following numbers :—

				Butyro-refractometer. Scale Divisions at 84° C., calculated to 40° C.
Commercial stearic acid	.	.	.	29·8-33 3
Japan wax	.	.	.	47·6-49·7
Carnaüba wax .	.	.	.	65·7-69
Beeswax	.	.	.	42·9-45·6

As a further preliminary test the *specific gravity* of the sample should be taken. The numbers recorded in the table (p. 920) will afford the necessary guidance. Of course, the specific gravity [5] test alone does

[1] *Chem. Zeit.*, 9, 1504.   [2] *Ibid.*, 1898, 730 ; *ibid.*, 1903, 808.
[3] *Ibid.*, 1898, 58.   [4] *Ibid.*, 1903, 752.
[5] Mastbaum (*Zeitschr. f. anal. Chem.*, 1902, 929) recommends a special contrivance for the determination of the specific gravity.

not give a final answer as to purity, since artificial compounds (see below) can easily be prepared so as to exhibit the specific gravity of a genuine beeswax.

The *melting point* of the sample should also be taken, although this test, either alone or in conjunction with the specific gravity, does not afford decisive information, inasmuch as mixtures having the specific gravity as also the melting point of genuine beeswax can be readily prepared.

The French codex in 1908 specifies the following test :—1 grm. of the sample is boiled for 30 minutes with 35 c.c. of a 15 per cent aqueous solution of sodium hydroxide, the water lost by evaporation being replaced. The liquid is then cooled and strained through absorbent cotton ; on the addition of hydrochloric acid no precipitate should be obtained. This test is said to indicate admixture with glycerides, resins, and other waxes. *Le Naour* [1] states, however, that this method is defective.

Stoeber [2] recommends the determination of the flash point (open test) as he found in the eleven samples of pure beeswax values lying between 212 and 250° C., whereas most adulterants flash below 200° C. with the exception of carnaüba wax which flashes at 316° C. A mixture of 90 parts carnaüba wax and 10 parts ceresin has a flash point like that of beeswax.[3]

Most important clues for the detection of adulteration are furnished by the determination of the *acid value* and of the *saponification value.*

The determination of the *acid value* is carried out in the usual manner (described Vol. I. Chap. VI.), by warming 3 to 4 grms. of the sample with 20 c.c. of 96 per cent alcohol in a flask until the wax is melted, distributing the wax by shaking, and titrating with standardised (about half-normal) alcoholic potash, phenolphthalein being the indicator. Care must be taken that the wax remains in a melted state during the operation. If the solution is diluted with a large quantity of alcohol and kept hot, the acid value may also be determined with half-normal aqueous alkali.

The determination of the *saponification value* should be carried out with a separate quantity of wax, as unless strongest alcohol has been used in the determination of the acid value, the saponification of the wax is not easily completed. It has been pointed out already that waxes are not saponified with the same facility as are oils and fats. The difficulties encountered by some analysts in saponifying beeswax have led to a number of proposed modifications, which are altogether unnecessary if the saponification be carried out with strongest alcohol, not containing more than 3 to 4 per cent of water. The wax should be saponified with alcoholic potash prepared with alcohol of at least 96 per cent strength. Even then the saponification cannot be considered as complete after half an hour, as experiments instituted in the author's

[1] *Ann. Chim. analyt.*, 1909, 369.
[2] *Chem. Zeit* . 1909, 146.
[3] Stockrer, *Chem. Zeit.*, 1908, 1275.

laboratory showed that after that time saponification values of only 60 were obtained, whereas if the wax was boiled with alcoholic potash over free fire for an hour complete saponification was effected.[1] It is advisable before titrating back with acid to add 30-40 per cent of alcohol. Complete saponification is still more readily reached by employing sodium alcoholate (cp. Vol. I. Chap. II.).

Henriques' process of cold saponification does not offer any advantage. The employment of caustic soda causes difficulties, the soda soaps of beeswax fatty acids being less readily soluble than the potassium salts. Indeed, *Henriques* later on modified his method by proposing to use petroleum ether of a boiling point of not less than 120° C., and to boil the solution of wax in such petroleum ether with alcoholic caustic soda, previous to allowing to stand. The necessity of operating with a boiling solution entirely disposes of the possibility of saponifying "in the cold." It may, however, be added that correct results can be obtained by first boiling and then allowing to stand.

Buchner[2] recommends to boil in an Erlenmeyer flask attached to a Soxhlet extractor, so that concentration of the alcohol may take place intermittently.

In pure beeswax the amount of free fatty acid stands in a definite proportion to the amount present in the form of combined esters. This was pointed out first by *Hehner*,[3] and independently and almost simultaneously by *Hübl*.[4] *Hehner* calculated the amount of alkali used for determining the free fatty acids to "cerotic"[5] acid, on the assumption that 1 c.c. of normal KOH neutralises 0·410 grms. of free acid. The alkali used for the saponification[6] of the neutral esters—*i.e.* the difference between the saponification value and the acid value—was calculated by him to "myricin,"[5] on the assumption that 1 c.c. of normal KOH saponifies 0·676 grm. of myricin.

In the following table a number of *Hehner's* analyses are collated :—

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[1] It is unnecessary to boil 4-8 hours, as recommended by *Berg.* In order to carry out the saponification at a higher temperature Eichhorn (*Zeitschr. f. anal. Chem.*, 1900, 39, 640) employs amyl alcohol as a solvent. Of course, the amyl alcohol must be pure, *i.e.* must not contain free acid nor esters, nor basic substances. Cp. also Berg, *Chem. Zeit.*, 1909, 886.

[2] *Chem. Zeit.*, 1905, 332.   [3] *Analyst*, 1883, 16.

[4] *Dingl. Polyt. Journ.*, 1883 (249), 338.

[5] The inverted commas do not occur in the original paper ; they have been added here by the author in order to avoid confusion with the chemical individuals *cerotic acid* and *myricin*.

[6] Becker (*Zeitschr. f. analyt. Chem.*, 19, 241) was the first to employ saponification in the examination of beeswax.

Kind of Wax.	"Cerotic Acid."	"Myricin."	Total.
	Per cent.	Per cent.	Per cent.
Wax from Hertfordshire . .	14·35	88·55	102·90
,, ,, .	14·86	85·95	100·81
,, Surrey . . .	13·22	86·02	99·24
,, Lincolnshire . .	13·56	88·16	101·72
,, Buckinghamshire .	14·64	87·10	101·74
,, Hertfordshire . .	15·02	88·83	103·85
,, New Forest . .	14·92	89·87	104·79
,, Lincolnshire . .	15·49	92·08	107·57
,, Buckinghamshire .	15·71	89·02	104·73
,, America . . .	15·16	88·09	103·25
,, Madagascar . .	13·56	88·11	101·67
,, Mauritius . .	13·04	88·28	101·32
,, ,, . .	12·17	95·68	107·85
,, ,, . .	13·72	96·02	109·74
,, Jamaica . . .	13·49	85·12	98·61
,, ,, . .	14·30	85·78	100·08
,, Mogadore . .	13·44	89·00	102·44
,, Melbourne . .	13·92	89·24	103·16
,, ,, . .	13·18	87·47	100·65
,, Sydney . . .	13·06	92·79	105·85
,, ,, . .	13·16	88·62	101·78

Hübl expressed the results of the examination of beeswax by simply stating the acid value and the saponification value in terms of mgrms. KOH (cp. Vol. I. Chap. VI.). The acid values of a number of samples of yellow wax were found by *Hübl* from 19 to 21, mostly 20; and the saponification values from 92 to 97, mostly 95. *Hübl*, being of the opinion that as a rule the higher and lower values occur simultaneously, assumed that the amount of free fatty acids stood in a definite—almost constant—ratio to the amount of esters. He therefore brought the amount of alkali required for neutralising the free acid—*i.e.* the acid value—into numerical relation to the amount of alkali required to saponify the neutral esters. The difference between the saponification and the acid value was termed by him "ether value." (For reasons stated Vol. I. Chap. VI., the term "ether value" or "ester value" has been abandoned in this work.) This ratio is 20 : 75 = 3·75 (75 being the difference between the saponification value, 95, and the acid value, 20). *Hübl* found in a number of beeswaxes that this "ratio number" varied between 3·6 and 3·8, and he therefore assumed that a beeswax, the "ratio number" of which deviates much from 3·7, must be looked upon as adulterated.

From *Hehner's* numbers given above the "ratio number" 3·9 can be calculated; this is in satisfactory agreement with *Hübl's* ratio number 3·75.

Hehner's mode of expressing the results in terms of "cerotic" acid and "myricin" is not adopted in this work, and should be abandoned as resting on assumptions, the correctness of which cannot be admitted at present. It may be conceded that the mean molecular weight of 410 for "cerotic" acid of beeswax (theory 396 for cerotic acid) is quite admissible, for the author actually found in several experiments the

molecular weights of the isolated acids to be from 405·6 to 419. But the calculation of the alkali used for saponification of the neutral esters to myricin is not permissible since the proportions of hydrocarbons in " normal " beeswaxes have been shown to reach as high a percentage as 13 to 17 per cent. Hence the numbers calculated for " myricin ", include, besides true myricin, varying amounts of hydrocarbons, so that the average number " 88 " given for " myricin " would represent only about 73 to 75 per cent of true myricin and 15 to 13 per cent of hydrocarbons, provided no free alcohols (see above, p. 900) were present. It need hardly be pointed out that the definite iodine value of beeswax entirely precludes the assumption that myricin alone, or even a mixture of myricin and free myricyl and ceryl-alcohols alone, occurs in the neutral portion of beeswax.

Hübl's numbers, on the contrary, merely express analytical data, such as are found by direct experiment. *Hübl's* " ratio number " introduces no further assumption, since it is derived from the data obtained by two titrations.

Ryan,[1] independently of *Hehner*, proposes a method based on the assumption that the molecular weight of cerotic acid is higher than that of any other free acid that may occur in mixtures. The method is as follows :—4 grms. of the wax are heated with 60 c.c. of neutral absolute alcohol and titrated with half normal alcoholic potash. The alcoholic mixture is mixed with 40 grms. of dry sand, and evaporated to dryness. The residue is extracted with petroleum ether and the extract dried and weighed. The difference between 100 and this weight gives the percentage of free acids, and from these figures their acid value can be calculated. Assuming that the acids other than cerotic are palmitic and stearic, the amount of cerotic acid can be calculated, and from that figure the amount of beeswax in the mixture can be approximately estimated. The method breaks down, however, as *Ryan* himself points out, if montan wax containing montanic acid is present.

In order to emphasise the importance of the " ratio number " for the detection of adulteration, I collate in the following table the " ratio numbers " of some substances that are likely to be used in the adulteration of beeswax. It should be observed that the acid values are arbitrarily assumed mean values.

[1] *Proc. Royal Dublin Soc.*, 1909, 210.

[TABLE

Substance.	1 Acid Value.	2 Saponification Value.	3 Difference, 2-1.	4 Ratio of 1 J. "Ratio number."
Carnaüba wax . .	2	80	78	39
Japan wax . . .	20	227	207	10·8
Insect wax . . .	3	80·4	77·4	29·1
Spermaceti . .	Traces	130	130	...
Myrtle wax . . .	3	208	205	68·3
Tallow	4	195	191	48
Stearic acid, pure .	195	195	0	...
,, ,, commercial	200	200	0	...
Rosin, Austrian . .	130·146	146·8-167·1	16·4-21·1	0·126-0·144
,, American . .	154·1-164·6	183·6-194	29·5-30·0	0·191-0·182
Galipot	138	174·6	36·1	0·261
Paraffin wax, ceresin [1] .	0	0	0	...

Buchner and Fischer [2] state that Ghedda wax may be differentiated from the wax of *Apis mellifica*, not only by the low proportion of free acids and correspondingly high amount of esters (ratio number), but also by the fact that Ghedda wax contains only one alcohol, namely, ceryl alcohol in contradistinction to the ordinary beeswax in which the alcoholic constituents consist chiefly of myricyl alcohol with a little ceryl alcohol.

This is confirmed by *Buchner and Deckert*, who determined the acetyl value by the mixed alcohols and hydrocarbons. These authors state that the acetyl value of the unsaponifiable matter from ordinary beeswax is fairly constant at about 122. The acetyl value of pure ceryl alcohol is 132·3, and that of myricyl alcohol 116·9 (cp. Vol. I., p. 431).

Fischer [3] further states that the analytical limits for Ghedda wax must be allowed greater latitude than for the wax of *Apis mellifica*.

According to *Emmanuel* [4] the ratio numbers of beeswaxes from Greece are slightly higher than the normal.

Like the East Indian waxes, the beeswaxes from China and Japan show a low acid value and a correspondingly high ratio number. These Japanese and Chinese waxes are of better quality, showing evidence of more care being used in their preparation than is the case with Indian waxes. They are also more readily bleached by sunlight.

According to *Fischer* [5] the waxes from China and Japan frequently contain paraffin wax. According to the same author the persistent emulsions obtained in the treatment of Indian beeswax is due to the borax which has been used in their purification. These waxes are sometimes adulterated with " rosin wax," *i.e.* a mixture of colophony and paraffin wax. For the detection of these adulterants, see below,

[1] Commercial paraffins or ceresins, however, may have a definite acid value.
[2] *Zeitschr. f. öffentl. Chem.*, 1913, 147.
[3] *Ibid.*, 1913, 354.
[4] *Berichte d. Dent. Pharm. Ges.*, 1913, vi.
[5] *Zeitschr. f. öffentl. Chem.*, 1913, 473.

pp. 923, 924. East Indian wax invariably contains some proportion of the wax from the Indian Dammar bee, *Trigona laeviceps*, cp. p. 916.

The acid and saponification values, the means of which have been given already, as also the "ratio numbers," are fairly constant for genuine beeswaxes collected from all parts of the world with the exception of those from India and China (Annam). This will be gathered from the following table, in which I have collated a large number of observations, which may be taken as representative of the beeswaxes obtainable from the localities named :—

Origin	Number of Samples	1. Specific Gravity at 15° C.	2. Melting Point °C.	3. Butyro-refractometer "degrees" determined at 84° C calculated to 40° C	4. Acid Value	5. Saponification Value	6. Difference, 5-4	7. "Ratio Number."	8. Iodine Value	9. c.c. ¹⁄₁₀ nor. KOH required for acids soluble in 80 per cent alcohol.[1]	10. Hydrocarbons. Per cent	Observer.
Abyssinia, crude	.	0·958	65	...	20·8	93·5	72·7	3·5	...	...	...	Dietze
,, remelted		0·958	64·2	...	18·9	94·6	75·7	4·0	...	...	...	,,
,, Max.	5	...	61·5	44·7	21·00	101·50	80·78	4·03	12·66	5·04	...	Berg
,, Min.		...	63·5	44 5	19·94	96·39	76·40	3·83	10·41	4·14	...	Berg
Algeria	28	0·960	63·5	44·6 14·8	20-20·5	98·5-99·5	78·5-79	3·8-3·9	9·10·5	4·5-4·6	...	Dietze
Angola	...	...	63·5	...	19·6	92·9	73·3	3·7	...	...	...	Berg
Argentina Max.	4	...	64·0	44·1	19·89	97·62	78·02	3·96	9·60	3·28	...	Berg
Min.		...	64·5	43·9	19·39	96·40	76·86	3·85	9·42	3 14	...	
Australia Max.	4	...	64·0	44·3	19·25	96·95	77·70	4·04	9·71	2 24	...	Berg
Min.		...	64·5	43·9	18 76	94 61	75·08	4·00	9·23	2·02	...	,,
Belladi	24	0·961	64·5	44·2	20·50	95·5-98·5	76·0-78·0	3·6-3·7	8·7-9·5	3·2-3·3	...	Dietze
Benguela		...	63	...	19·3	93·1	73·8	3·8	...	...	...	Dietze
,, Max.	4	...	64·0	45·9	20·58	97·51	77·07	3·80	11·31	4·82	...	Berg
,, Min.		...	63·5	45·2	20·31	97·02	76·93	3·74	10·76	4·79	...	Dietze
Bissao Max.		0·959	65·5	44·8	20·9	95·4	74·5	3·6	...	...	...	Berg
Bissao Wadda Min.	2	...	65·0	44·6	21·14	99·89	78·89	3 77	11·32	4·48	...	Dietze
,,		...	63·5	...	20·93	99·82	78·75	3 72	19·68	4 26	...	Dietze
Brazil, I.	...	0·962	63·5	...	19·6	89·5	69·9	3·6	...	...	...	Berg
,, II.		0·963	63·5	...	18·3	90·5	72·2	3·9	...	...	...	,,
,,	47	...	65·5	43·5	18 9·19 2	96·0-96·5	76·5-77·5	4·0-4·1	9·0-9·5	2·5-2·6	...	Berg
Caiffa Max.	2	...	65 0	44·6	20·28	99·26	79·10	3·92	7·98	3·36	...	,,
Min.		...	65·5	44·4	20·16	99·10	78·82	3·89	7·39	3·14	...	
California Max.	5	...	65·0	44·1	19·11	95·31	76·72	3·99	10·76	3·58	...	,,
Min.		...	65·0	44·0	18·90	94 15	75·25	3·98	9·60	3·42	...	
Casablanca		0·959	63·5	...	18·6	94·8	76·2	4·1	...	...	...	Dietze
Max	5	...	63·5	44·6	21·14	100 94	81·06	4·08	13·01	5·15	...	Berg
Min.		...	63·0	44·4	19·88	99 17	79·17	3·75	9 56	4·93	...	
Chili		...	65	...	19·7	91·4	71·7	3 6	...	...	...	Dietze
,,	21	0·960	64·5	43·6	19·5-20·0	94·5-96·0	73·5-76·0	3·7-3·8	7·0	2·9-3·0	...	Berg

[1] 50 c.c. of filtrate from 5 grms. of beeswax.

Origin.	Number of Samples.	1 Specific Gravity at 15° C.	2 Melting Point ° C.	3 Butyro-refractometer "degrees" determined at 84° C. calculated to 40° C	4 Acid Value.	5 Saponification Value.	6 Difference, 5-4.	7 "Ratio Number."	8 Iodine Value.	9 c.c. ¼ nor KOH required for acids soluble in 80 per cent. alcohol [1]	10 Hydrocarbons. Per cent.	Observer.
Chili	...	0·965	...	...	18·81	90·10	71·29	3·79	...	2·00	15·1	Ahrens & Hett
Corsica	1		66·5	44·1	19·74	97·79	78·05	3·95	10·82	5·16	...	Berg
Cuba	...	0·961	64		20·2	95·2	75·0	3·8		...	...	Dietze
Cuba Max.	3		65·0	44·6	19·04	99·89	80·85	4·24	10·98	3·14	...	} Berg
,, Min.			64·0	44·0	18·20	93·24	75·04	4·12	9·46	2·12	...	Dietze
Domingo, pale	...	0·962	63·5	...	19·8	93·5	73·7	3·7	...		...	,,
,, dark	...	0·960	63·5	...	20·3	94·4	74·1	3·65	...		...	,,
,, commercial	...	0·960	65·0	45·1	20·0	93·8	73·8	3·7	10·82	4·59	...	} Berg
,, commercial Max.	5		65·0	44·6	21·63	97·79	77·42	3·91	9·84	2·68	...	Abr. a. Hett
,, Min.					19·81	94·64	74·69	3·52		2·69	...	Dietze
East Africa, German	...	0·967	64	44·9	20·11	93·45	73·34	3·65	9·99	5·82	...	Dietze
,, ,, German Max.	4	0·965	64·5	44·3	20·9	93·3	73·3	3·9	8·38	4·03	...	} Berg
,, ,, Min.	2		63·0		21·56	102·41	80·85	4·16	6·1-7·5		14·25	Fendler
Egypt	1	0·9489-0·9645	62·2-62·5	44·0	17·48-18·20	84·34-89·80	66·16-72·32	3·6-4·1	7·93	2·80	...	Berg Dietze
Germany	1427	0·960-0·961	63·5-61·5	44·8-44·7	19·2-20·4	92·0-97·0	72·0-77·0	3·6-3·8	7·5-8·0	2·6-3·3		} Berg / Ahr. a. Hett
,, Bayern		0·964	63·4		18·67	90·30	71·53	3·84			15·2	,,
,, Hanover		0·66	63·5		19·08	91·20	72·12	3·78			15·2	,,
,, Hessen		0·964			19·15	91·89	72·74	3·80			17·3	,,
,, Holstein	...	0·965			20·40	93·85	73·45	3·65		4·70	15·3	} Buchner
,, Max.	14				20·44	92·35	71·91	3·50		4·34	...	
,, Min.					18·29	91·29	73·00	3·99			...	
Greece Max.	...	0·967	65·75	...	20·43	101·5	82·2		10·9	...	...	} Emmanuel
,, Min.		0·958	63·25		16·82	86·3	67·5		6·7		...	
Haiti Max.	4		65·5	43·9	20·16	97·51	77·42	3·85	9·19	3·02	...	} Berg
,, Min.			64·5	43·9	20·09	93·45	73·29	3·02	8·46	2·13	...	
Italy	77		64·5	44·5-44·9	21·21·5	98·0-99·0	75·77·5	3·5-3·8	10·75-12·75	5·0-6·60	...	,,

Country		No.	Sp. gr.										Authority
Madagascar			0·960	61	44·7·45	21·1	98·0	76·9	3·65	9·0-10·0	4·0-4·?	...	Dietze
,,		18	...	64·5-65	15·5-19·5	20·30	97·0-101·0	78·0-81·0	+0·43	...	5·91	12·8	Berg
Mazagan, I.			0·970	64	...	21·7	96·80	76·50	3·77	...	...	...	Ahr. a. Hett
,, II.			0·962	64	...	22·0	102·8	81·0	3·8	...	...	...	Dietze
Mogador		184	0·962	63·5	44·4·45·0	19·6·21·5	96·5·98	76·5-78·5	3·8-4·0	10·5-12·0	5·25-4·5	...	Berg
Montenegro			0·960	64	...	20·2	92·7	72·5	3·6	...	...	...	Dietze
Morocco		212	0·968	63·5	44·7·45·2	19·8·21·3	95·5-98·0	75·5-78·5	3·75-3·95	10·5-12·7	5·3-6·1	13·2	Berg
Mozambique			0·958	...	...	20·4	98·89	74·0	3·72	...	3·80	...	Ahr. a. Hett
,,		1	0·967	63	44·7	20·94	94·0	81·76	3·7	11·32	3·58	13·1	Dietze
Northern Nigeria	Max	7		64·5	...	20·23	101·99	76·10	4·04	9·5	3·58		Berg
	Min					20·0	94·90	76·4	4·05	5·9	3·80		Imp. Inst.
Palenzia				65	...	20·0	96·3	75·3	5·0	5·9	...	...	,,
Palestine	Max	3		63·5	44·2	15·6	93·8	75·60	3·9	12·05	4·26	...	Berg
	Min			64·0	44·3	19·40	95·00	81·99	3·80	9·65	3·81	...	,,
Poland and Galicia	Max	19	0·966	65·5	43·9	21·70	103·69	81·13	3·77	9·27	3·36	15·0	Ahr. a. Hett
	Min			65·0	43·2·43·7	21·56	102·69	76·5-78·0	3·74	6·5-6·9	5·2-3·6		
Portugal	Max	17	...	63·5		19·2·19·5	96·0-97·5	73·47	3·9-4·0	14·0	4·48		Mastbaum
	Min			65·5		18·37	91·84	77·78	4·00	6·7	3·7		Berg
Sierra Leone		1		61·0	44·5	16·?1	88·54	70·49	4·30	8·50	1·1	...	,,
Smyrna		1		64·0	44·3	21·28	101·86	80·08	3·61	10·84	3·02	...	,,
Spain	Max	5		64·5	44·6	19·67	97·58	76·30	3·76	10·95	3·58	...	Dietze
	Min			66·5	44·3	19·32	98·70	79·38	3·58	10·76	3·70	...	,,
Sweden		1	0·959	63·5	43·9	20·09	96·04	76·65	4·11	9·35	3·25	...	,,
Tangier, I.			0·959	63	...	20·6	96·81	76·72	3·94		3·02	...	Dietze
,, II.			0·961	63	...	20·6	99·4	77·8	3·82			...	,,
Tunis		1		64	44·5	20·2	100·3	79·7	3·8			...	Berg
,,		33	0·965-	65·0		18·90	95·3	74·9	3·9	9·72	3·59	...	Bertain-chand [2]
,,			0·972	61·64		16·8·20	89·7-96·0	69·7-81·2	3·83	6·7-7·12			Ahr. a. Hett
Turkey	Max		0·965	65·0	43·4	19·60	92·18	72·58	3·43-4·50		3·36	15·0	Berg
	Min			64·5	42·9	20·30	96·67	87·28	3·70	9·11	2·34		
Valdivia	Max	5		65·0	44·4	19·59	95·11	75·81	3·98	8·37	2·12	...	Ahr. a. Hett
	Min					20·09	96·32	76·23	3·87	10·25	4·36		Dietze
West Africa, German		1	0·967		...	19·71	92·40	72·69	3·79		4·90	13·6	
Zanzibar			0·959	63	...	19·9	94·9	75·0	3·69				

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[1] 50 c.c. of filtrate from 5 grms. of beeswax.   [2] *Bull. de la Direction de l'Agricult. et du Commerce*, Tunis, 1898.

Most of the "ratio numbers" given in the last table lie in the neighbourhood of 3·8. From these "ratio numbers" the following conclusions may be drawn : If the saponification value of a sample of beeswax be below 92, whilst the "ratio number" is that of a pure beeswax, then *paraffin wax* or *ceresin* must be present. If the ratio number exceeds 3·8, then an admixture with Japan wax, tallow, insect wax, carnaüba wax, or spermaceti may be suspected. If the acid value be much below 20, then Japan wax is absent. If, however, the "ratio number" is less than 3·8, then "stearic" acid or rosin is present. From the foregoing table it will, however, be gathered that the "ratio number" is not so constant as has been assumed by *Hübl*. This is especially shown by the analyses of some genuine European waxes which I collate in the following table :—

Origin of Beeswax.	1	2	8	4	Observer.
	Acid Value.	Saponifica-tion Value.	Difference. 2-1.	"Ratio Number."	
Hungary . .	23	90·6	67·6	2·89	Mangold
Silesia . .	17·8	92·3	74·5	4·2	Weinwurm

It must further be borne in mind that at present artificial combs containing stearic acid are being employed in bee-hives. Hence the acid value of beeswax may be found higher. Beeswaxes obtained from such artificial honeycombs gave acid values ranging from 25 to 26 (*Weinwurm*).

All the foregoing numbers refer to yellow wax. Through bleaching, the yellow wax undergoes some changes which cause great deviations from the normal acid and saponification values. This is illustrated by the numbers I have collated in the following table. They show the changes which occur in the physical and chemical characteristics of yellow wax on being bleached by various methods. (Cp. also table, p. 920.)

	1 Melting Point °C	2 Acid Value	3 Saponifica- tion Value	4 Difference, 3-2.	5 "Ratio Number."	6 Iodine Value.	7 1 grm. yields Hydrogen. c.c.	8 Hydro- carbons. Per cent.	Observer.
Pure yellow waxs .	63-64	19-21	91-95	72-74	3.78-3.52	10-11	52.5-55	13-14	Buisine
Air-bleached waxes, with addition of 3.5 per cent of tallow	63.5-64	21-23	105-115	84-92	4.00-4.00	6.7	53.5-57	11-12	,,
Pure yellow wax	63.5	20.17	93.5	73.33	3.63	10.9	53	13.5	Buisine
Same wax air-bleached, with addition of 5 per cent of oil of turpentine .	63.5	20.2	100.4	80.2	3.97	6.8	54.9	12.4	,,
Same wax, bleached by hydrogen per oxide .	63.5	19.87	98.4	78.53	3.90	6.3	56.1	12.5	,,
Pure yellow wax	63	20.40	95.1	74.70	3.66	11.2	54.5	14.3	Buisine
Same wax, decolourised by animal char .		19.71	93.2	73.49	3.72	11.4	53.6	13.3	,,
,, ,, bleached with permanganate .	63.7	22.63	103.3	80.67	3.56	2.6			,,
,, ,, bichromate .	63.5	21.96	99.2	77.24	3.51	5.8	55.5	13.8	,,
,, ,,	63.2	21.86	98.9	77.04	3.52	7.9	51	13.2	,,
	64	23.43	107.7	84.27	3.59	7.1	53.6	11.8	
Beeswax, white	...	22.4	95.5	76.1	3.41	...	...	...	Henriques Allen Buchner[1]
,, chemically bleached	...	24	95.	71.95	2.96	...	...	...	,,
,, air-bleached	...	19.87	94.82	74.95	3.77	...	...	...	,,
,, chemically bleached. I.	...	22.02	98.17	76.15	3.45	...	...	...	,,
,, ,, II.	...	24.0	98.56	74.56	3.10	...	...		,,
,, before bleaching		20	95.1	75.1	3.7				
,, after bleaching	...	25.1	95.1	70.0	2.8	...	...	...	
Japanese wax from Fukuska .	65.8	6.27	93.13	86.86	13.85	16.70			Sokitln Shibasaki[2]
,, ,, bleached .	65.7	6.20	95.87	92.67	14.95	4.12			

[1] Buchner, Chem. Zeit., 1905, 32. The bleaching method employed is not stated.   [2] Private communication from Tsujimoto.

"Ratio numbers" differing enormously from those given above are found in Indian and Chinese (Annamite) waxes.

A number of analyses of such beeswaxes are collated in the following table:—

Origin.	Number of Samples.	1 — Specific Gravity at 15°C.	2 — Melting Point °C.	3 — Butyro-refracto-meter, determined at 84°C, calculated to 40°C	4 — Acid Value.	5 — Saponification Value.	6 — Difference, 5-4.	7 — "Ratio Number."	8 — Iodine Value.	9 — c.c. ½ norm. KOH required for acids soluble in 80 per cent alcohol, by Buchner's process.	Observer.
East India[1]	...	...	65	...	6·10	83·30	77·20	12·1	10	1·5	Buchner
,, Max.	418	...	66	...	6·01	82·12	76·11	12·6	10	1·5	,,
,, Min.		...	63·5	44·8	8·96	106·10	99·45	14·95	9·29	3·00	Berg
,, Mean		...	63·5	44·1	6·30	93·59	86·24	10·00	7·16	2·25-2·75	Buchner
,, Max.	132	...	63·0	44·3-44·7	7·0-7·5	96·0-101·5	89·0-94·0	12·5-13·5	8·5-8·7	2·02	,,
,, Min.		...	...	...	12·2	106·1	...	15·2	...	?	
Tonkin and Cochin-china Max.	281	...	63·5	45·1	5·3	81·77	89·88	7·4	9·07	3·58	Berg
,, Min.		...	63·0	44·7	8·41	97·02	85·73	12·33	6·96	2·67	Bellier[2]
Annam	,	0·964	61	45·5	7·21	93·27	...	11·40	6·0	...	Berg
China[3] Max.	4		66·5	45·4	7·8	94·4	96·88	...	12·17	6·16	Buchner
,, Min.			66·0	...	9·52	105·07	94·85	10·02	11·98	6·08	
,,	...		66	...	9·03	104·37	86·15	9·96	...	...	
,, Max.			62-63	...	7·55	93·70	90·28	11·4	...	...	
,, Min.			...	...	5·33	95·61	111·45	17·9	...	...	
,, Max.			...	...	8·72	120·17	83·82	12·78	...	...	
,, Min.			...	...	6·28	90·20	80·74	13·9	...	...	
Japan[4] Max.	13	0·8135	64·9	...	5·61	86·35	...	11·19	10·18	...	Sokichi Shibassaka
,, Min.		0·8207	66·5	...	8·19	103·33	95·14	14·60	14·14	...	

Indian from *Apis florea*	5										D. Hooper[5]
Max.		0 953	68	…	8·9	130·5	121·6	13·66	11·4	…	„
Min.		…	63	…	6·1	88·5	82·4	13 5	6·6	…	„
Mean		to	64·2	…	7·5	103 2	95·7	12 76	8·0	…	„
„ *Apis dorsata*	22										„
Max.		…	67	…	10·2	105·0	94·8	9 29	9·9	…	„
Min.		…	60	…	4·4	75·6	71·2	16·1	4·8	…	„
Mean		0·964	63·1	…	7·0	96·2	89·2	12·7	6·7	…	„
„ *Apis indica*	7										„
Max.		…	64	…	8·8	102·5	93·7	10 64	9·2	…	„
Min.		…	62	…	5·0	90·0	85·0	17·0	5·3	…	„
Mean		…	63·25	…	6·8	96·2	89·4	13·1	7·4	…	„
„ *Trigona*, Sp.	8	Dammar or *Kotabu*									„
Max.		…	76	…	22 9	150 0	127·1	5·5	49·6	…	„
Min.		…	66	…	16·1	73·7	57·6	3·57	30·2	…	„
Mean		…	70·5	…	20·8	110·4	89·6	4·34	42·2	…	„
„ *Apis dorsata*[6]	…	0·9	62	…	6·7	97·7	91·0	13·6	8·9	…	Heymann[7]

[1] To this class of waxes belongs the wax known in commerce as "Ghedda wax." The proportion of hydrocarbons is, as a rule, 8·6 per cent (Buchner, *Chem. Zeit.*, 1905, No. 7).

[2] *Ann. chim. analyt. et appl.*, 1906 (11), 366.

[3] Not to be confounded with Chinese insect wax.   [4] Not to be confounded with Japan wax.

[5] *Agricultural Ledger*, Calcutta, 1904 (7), p. 73.   Cp. also Buchner, *Chem. Zeit.*, 1906, No. 43.

[6] In Wenwurm test, perfectly clear.   [7] Determined in the author's laboratory.

Ghedda wax differs from ordinary beeswax by a characteristic toughness and plasticity as also by a lower solidifying point, which lies between 59-58·5°.

Ghedda wax differs also chemically from beeswax in that it only contains one alcohol, viz. ceryl alcohol, which occurs in the form of an ester, whereas the ordinary beeswax contains chiefly myricyl alcohol and very little ceryl alcohol. The Ghedda wax appears also to differ from ordinary beeswax by containing other fatty acids, as will be shown by *Lipp and Kühn* in a future publication.

The hydrocarbons in Ghedda wax melt between 62°-70° C. *Lipp and Kühn* [1] isolated a hydrocarbon melting at 70° C. probably having the composition $C_{30}H_{64}$. A second hydrocarbon was isolated melting at 63·5° C., and a third melting at 58·0° C., having probably the composition $C_{26}H_{54}$.

Ghedda wax responds readily to the ordinary bleaching agents. This wax has a lower acid value and a correspondingly higher ratio number than ordinary beeswax (cp. *Buchner and Fischer*).[2]

Lipp and Kühn found acid values varying from 5 to 7·5, and ester values from 86-92 in a number of samples.

These beeswaxes were considered as "abnormal" since no adulterants could be detected by the usual tests. It can, however, not be doubted that the waxes from *Apis florea*, *A. dorsata*, and *A. indica*, enumerated in the last table, are genuine products of the bee. The so-called black wax of Burma,[3] termed locally "Pwê-nyet," is a product of a stingless bee *Trigona laeviceps*, Smith (*Melipona laeviceps*, Dall), the Indian Dammar bee. Owing to either the inability of the bee to excrete ordinary beeswax, or to the quantity of the wax excreted being insufficient for the building of a proper hive, or because the quality of the wax excreted is such that a hive cannot be built from it, the "Pwê-nyet" seems to be a mixture of such beeswax as the *Trigona* species excrete, with dammar resins. In fact the term Pwê-nyet is applied to both the bees' secretion and to dammar resins obtained from the several species of *Dipterocarpus*, *Shorea*, *Hopea*, *Vateria*, and *Canarium*. The exterior portions of the nest consist of a resinous material the composition of which agrees in many respects with the dry resin of *Dipterocarpus tuberculatus*. The beeswax from *Apis dorsata*, described last in the foregoing table, is of undoubted genuineness; it was forwarded to the author by *D. Hooper* from Calcutta as wax separated from the comb of the *Apis dorsata* from Saharanpur, United Provinces. Some of those waxes (sold as Chinese) seem to be mixtures of genuine beeswax with (Chinese) insect wax. At least, in the case of a sample of Chinese beeswax submitted to me for examination I was able to prove that adulteration with (Chinese) insect wax had taken place. The numbers obtained in the course of the usual examination are given in the following table :—

[1] *Journ. f. prakt. Chem.*, 1912 (86), 184.
[2] *Zeitschr. f. offentl. Chem.*, 1913, 147.
[3] D. Hooper, *Agric. Ledger*, 1909, 81.

Specific Gravity at 15°.	Acid Value.	Saponification Value.	"Ratio Number."	Iodine Value.
0 9392	9·61	87·62	8·73	11 53
At 100°.				
0·8555				

Buchner[1] found two samples from Spain and Italy to have ratio numbers from 2·9 to 3·1, and suggests that they may both have come in the first place from Africa.

Normal acid and saponification values alone do not furnish sufficient proof of the purity of a beeswax, as it is easy to prepare mixtures having a normal " ratio number " and yet containing no beeswax whatever. This will be gathered from the following table, which gives the acid and saponification values for a mixture consisting of 37·5 parts of Japan wax, 6·5 parts of stearic acid, and 56 parts of ceresin or paraffin wax.

	1	2	3	4	5	6	7	8	9
						Conditioning			
	Acid Value	Saponification Value	Difference, 2-1.	"Ratio Number."	Parts in 100.	Acid Value.	Saponification Value.	Difference, 7-6.	"Ratio Number."
Japan wax	20	220	200	10	37 5	7·5	84·5	75	10
"Stearic" acid	195	195	0		6 5	12 7	12·7	0	...
Ceresin, paraffin wax	0	0	0		56 0	0	·0	0	...
Mixture						20 2	95·2	75	3·71

The ratio number of this mixture would be 3·71. It is evident that indefinite quantities of the above mixture, or of a similarly prepared one, might be added to beeswax without being detected by merely ascertaining the acid and saponification values.[2]

The determination of the iodine value is of somewhat secondary importance in the examination of beeswax; still, it will assist in the

[1] *Zeitschr. f. offentl. Chem.*, 1912, 90.

[2] As a rule such mixtures—known under the name "Composition waxes"—are coloured by the addition of colouring matter. P. Lemaire, *Bull. Soc. Pharm. de Bordeaux*, June 1904, suggests several methods for the detection of colouring matters.

interpretation of the results obtained by other methods, and in the detection of certain impurities.[1]

In doubtful cases further examination is required, and the following tests are recommended :—

Detection and Determination of Glycerides.[2]—Although in most cases the presence of glycerides will be detected by a higher saponification value than the normal one, still, small quantities may be introduced by means of a judiciously prepared mixture of glycerides, stearic acid, and paraffin wax or ceresin. The absence of glycerides can only then be pronounced upon with certainty if no glycerol is found. The safest plan is to determine the amount of glycerol quantitatively by working with at least 20 grms. of the suspected wax. The qualitative test for glycerol is too delicate, since small quantities, such as 2 to 3 per cent of a glyceride, which may have been admixed with a yellow wax before bleaching (as is usually done on a manufacturing scale), may give a positive reaction in the acroleïn test, and thus lead to erroneous conclusions. The acroleïn test must therefore be confirmed by quantitative tests. The amount of glycerol multiplied by 10 gives approximately the percentage of added glyceride.

Buchner states that traces of glycerides can be detected in pure beeswaxes.

Detection of Stearic Acid.—A considerable quantity of " stearic acid " is readily detected by a high acid value of the sample, provided no compensating substances like ceresin and paraffin wax have been added. It should be borne in mind that colophony also raises the acid value (for the detection of resin, see below). If in consequence of added paraffin wax or ceresin a normal acid value has been found, and yet stearic acid be suspected, then one of the following methods must be resorted to. They are based on the principle that on treating a sample with boiling alcohol any stearic acid present will be dissolved together with cerotic acid, but will not separate out so completely as the latter does on cooling. The following process has been suggested by *Fehling*,[3] and recommended by *Röttger*[4] : 1 grm. of the sample is boiled for a few minutes with 10 c.c. of 80 per cent alcohol ; after cooling, the alcoholic solution is filtered and the filtrate mixed with water. In the case of a pure beeswax the liquid is perfectly clear, or is only slightly opalescent, but in case of adulteration with stearic acid, the liquid loses its transparency, and flocks of separated stearic acid rise to the top. This reaction is plainly perceptible even if the added stearic acid be as little as 1 per cent. It should be borne in mind that rosin also, if present, will be dissolved, and give an emulsion with water.

[1] According to D. Hooper (*Agricultural Ledger*, 1904, No. 7), in one district of the Punjab the strained wax is intermixed with one-eighth of its weight of sesamé oil before it is made into lumps for the market.

[2] Thénard proposed to detect glycerides in beeswax by isolating sebacic acid from the products of dry distillation (cp. *Liebig's Annal.*, 1840 (35), 194). For a method depending on the colouration with copper sulphate cp. Wagenaar, *Pharm. Weekblad*, 1911, 479.

[3] *Dingl. Polyt. Journ.*, 147, 227.   [4] *Journ. Soc. Chem. Ind.*, 1890, 771.

Jean[1] endeavours to determine stearic acid quantitatively by heating 3 to 4 grms. of the sample with 60 c.c. of 96 per cent alcohol to boiling, allowing the solution to cool, and titrating with half-normal alkali, using phenolphthalein as an indicator. The alkali used is calculated to stearic acid.

In the presence of rosin the determination would include the amount of alkali required to neutralise the rosin acids.

A combination of these two tests has been more fully worked out by *Buchner*.[2] He proceeds in the following manner: 5 grms. of the sample are placed in a round-bottomed flask and 100 c.c. of 80 per cent alcohol (prepared from 850 c.c. of 96 per cent alcohol and 190 c.c. of water) are added. The total weight of the flask and contents is then ascertained. Next the contents of the flask are heated until the mass boils gently and are kept at this temperature for 5 minutes, with frequent shaking. The flask is then immersed in cold water whilst being constantly shaken and allowed to cool down to the ordinary temperature. The flask is weighed again and brought up to the original weight by the addition of 80 per cent alcohol. The liquid is then filtered through a plaited filter, and 50 c.c. of the filtrate are titrated with $\frac{1}{10}$ normal alcoholic potash, phenolphthalein being used as an indicator. By proceeding in this manner *Buchner* obtained the following acid values :—

	c.c. $\frac{1}{10}$ norm. KOH. required for acids soluble in 80 per cent alcohol. 50 c.c. of alcohol from 5 grms. of substance.
Pure beeswax, yellow	3 6·3·9
,, ,, white	3·7·4·1
Palm wax	1·7·1·8
Carnauba wax	0·76·0·87
Japan tallow (Japan wax) . .	14·93·15·3
Rosin	150·3
Stearic acid[3]	65·8
Tallow " stearine "	1·1
" Artificial waxes," having the " ratio numbers " of normal beeswax—	
I. Consisting of stearic acid, tallow stearine, and ceresin	21·40
II. Consisting of stearic acid, Japan tallow, and cerosin	17·80
III. Consisting of rosin, tallow stearine, and ceresin .	22·0
Pure beeswax, mixed with 25 per cent " Artificial wax " I.	8·4
,, ,, ,, ,, 50 ,, ,, ,, ,, II.	11·3

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[1] *Journ. Soc. Chem. Ind.*, 1891, 728.

[2] *Chem. Zeit.*, 1895, 1422.

[3] It must be pointed out that this can only refer to commercial "stearic" acid, as the pure acid exhibits much smaller values.

[TABLE

Physical and Chemical Characteristics of Beeswax [1]

Specific Gravity			Solidifying Point.		Melting Point			Acid Value.		Saponification Value.	
°C.		Observer.	°C.	Observer.	°C.		Observer		Observer.	Mgrms. KOH.	Observer.
15	0·965-0·975	Hager	60·5 [2]	Allen	63 [2]		Allen	20	Hubl	95	Hubl
,,	0·962-0·966 [2]	Dieterich-	62 [6]	,,	63 5 [6]		,,	18·6 [3]	Dieterich	90·4-91·4 [3]	Dieterich
,,	0·9627-0·9656 [3]	Lewkowitsch	62·5 [7]	Lewkowitsch	63·0·7		,,	16·8-20·6 [2]	,,	87-8-96·2 [2]	,,
,,	0·959-0·966 [4]	Camilla	60·5-62·8 [4]	Camilla	65 [3]		Barfoed	19·02-20·6·[2]	Buisine	97-107	Becker
,,	0·959 [5]	,,	61·9-63·1 [9]	Mastbaum	69·70 [3]		Lepage	19·04-20·9 [4]	Camilla	93·5-97 1 [2]	Lewkowitsch
,,	0·964-0·970	Hett and Ahrens			63-64·4 [4]		Camilla	20·9-21 2 [5]	,,	90·1-98·89 [2]	Hett and Ahrens
80	0·8356 [9]	Allen			62 5-63 6 [9]		,,	20·6-21·09 [2]	Lewkowitsch		
(water 15·5=1)								18·37-20·94 [9]	Hett and Ahrens		
98	0·8221 [6]	,,						17-21·8 [3]	Lewkowitsch	94·2-97·6 [3]	Lewkowitsch
98-99	0·827 [6]	,,									
,,	0·818	,,									

Physical and Chemical Characteristics of Beeswax—continued

Iodine Value.		Reichert-Meissl Value.		Alcohols+Hydrocarbons [10] (Unsaponifiable).		Refractive Index. At 75° C. 1·4398-1·4451 L. Feldstein [11].				Fatty Acids.	
							At 75° C. Butyro-refractometer.				
Per cent.	Observer.	c.c. 1/10 norm KOH.	Observer.	Per cent.	Observer.	"Degrees,"		Observer.		Per cent.	Observer.
8·3-11	Buisine	0·34-0·41 [4]	Camilla	55·25	Schwalb	42·9-45 6 determined at 84° C. calcul. to 40° C.		Berg		46·77 [12]	Lewkowitsch
7-9-8·9	Guyer [8]	0·54 [5]	,,	52·38	Allen and Thomson						
(see p. 908)	Berg			55·58 [2]	Lewkowitsch						

1 Cp. also tables, pp. 909-914.   2 Yellow wax.   3 White wax.   4 Italian waxes not Ligurian.   5 Ligurian wax from *Apis Ligustica spinola*.
6 Chemically bleached.   7 Air bleached.   8 Eleven samples of pure English waxes (*Journ. Pharm.* 1897, 308).   9 17 Portuguese waxes.
10 Specific gravity at 100° (water at 100°=1)=0·8239 (Archbut).   11 *Chem. Eng.*, 1912 (15), 211.   12 Melting point 67·2° C.

Berg,[1] who examined a very large number of waxes by *Buchner's* method (see table, p. 909), points out that the alcoholic solution made up as described above must be allowed to stand 12 hours, as otherwise the results are discordant, and generally too high. Unless a sample be allowed to stand 12 hours, the acids dissolved by the 80 per cent alcohol are found too high by 20 to 30 per cent. It should be further pointed out that the detection of stearic acid in bleached waxes, if present only to the extent of 1 to 3 per cent, is very difficult, as chemically bleached waxes may retain small amounts of acid substances.[2]

The author obtained for genuine yellow beeswax smaller numbers than did *Buchner*. Thus a Gambia beeswax required for neutralisation of the free acids extracted as described above 2·39 c.c. of decinormal alkali; the isolated acid had the mean molecular weight 406, whereas the same Gambia wax adulterated with varying quantities of " stearic acid " required of course much higher amounts of decinormal alkali, whilst the mean molecular weights of the isolated fatty acids varied from 274·8 to 298·8. In the latter case appreciable amounts of beeswax cerotic acid had passed into the alcoholic solution.

In doubtful cases it appears advisable to use larger quantities, then to separate the stearic acid as such,[3] and to examine it further. It need hardly be pointed out that commercial stearic acid, such as would be used for adulteration, is not pure stearic acid (cp. Vol. III. Chap. XVI.).

Buchner[4] states that on treating 3·6 grms. of beeswax after saponifying and evaporating off the alcohol with 250 c.c. of boiling water, some beeswaxes yield clear solutions, whereas others (East African, East Indian (Ghedda)) yield turbid solutions or amorphous precipitates. Waxes containing paraffin wax also yield turbid solutions, hence it is necessary to identify the separated substance. This appears to be tantamount to examining the unsaponifiable matter.

Detection of Ceresin and Paraffin Wax.—The examination of beeswax by the saponification process can only reveal the presence of more than 10 or 8 per cent of ceresin and (or) paraffin wax, if no other adulterant be present. If the admixture falls below 5 or even below 8 per cent, the deviations from the normal acid and saponification values become so small that by these two tests alone adulteration cannot be revealed. An excellent preliminary test for the detection of added ceresin and paraffin wax down to 3 per cent has been proposed as a qualitative test by *Weinwurm*.[5] This qualitative method is based on the fact that a hot aqueous glycerin solution dissolves the unsaponifiable matter of beeswax, whereas ceresin and paraffin wax are insoluble in it. The process is carried out as follows :—Saponify 5 grms. of the sample with 25 c.c. half-normal alcoholic potash (in a 200 c.c. flask), evaporate off the

[1] *Chem. Zeit.*, 1903, 754.
[2] Thus Medicus and Wallenstein (*Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1902, 1092) showed that the acid value of a beeswax bleached with bichromate and sulphuric acid was as high as 24·7 (cp. also table, p. 913).
[3] Cp. Berg, *Chem. Zeit.*, 1908, 779.
[4] *Zeitschr f. offentl. Chem.*, 1911, 225.
[5] *Chem. Zeit.*, 1897, 519.

alcohol completely, add 20 c.c. of concentrated glycerin, heat on the water-bath until solution is effected, and then run in 100 c.c. of boiling water. Pure beeswax gives a more or less clear, transparent, or translucent mass, through which ordinary print can be read easily. If 5 per cent of hydrocarbons are admixed, the solution is cloudy, and the print is no longer legible ; in the case of an admixture of 8 per cent of hydrocarbons a precipitate is obtained.

I have examined this process in my laboratory, and can recommend it as a reliable preliminary test for *pure beeswax*. Turbidity of the solution does not, however, solely indicate the presence of added ceresin or paraffin wax, since carnaüba wax and insect wax also give a turbid solution. Mixtures prepared from pure beeswax and carnaüba wax, as also mixtures from pure beeswax and (Chinese) insect wax, give as strong a turbidity as does pure beeswax containing 5 per cent of added paraffin wax (*Lewkowitsch*). Beeswax from *Apis dorsata* remains clear in the *Weinwurm* test (*Lewkowitsch*). *Berg*[1] states, however, that some East Asiatic and South Asiatic beeswaxes containing considerable amounts of melissyl (myricyl) alcohol almost invariably give a turbidity in *Weinwurm's* test.

In doubtful cases it is best to prepare for guidance solutions made up with pure beeswax and with mixtures thereof and the suspected adulterant.

Sokoloff[2] suggests the determination of the *heat of combustion* of the sample as a method of detecting small quantities of paraffin wax. Genuine beeswaxes give a heat of combustion of 10,312 calories, whereas paraffin and ceresin gave on an average 11,234 calories. Evidently this method is a very cumbersome one, and cannot therefore be recommended.

The specific gravity test will only reveal considerable quantities of added ceresin and paraffin wax, and therefore discriminative importance cannot be assigned to it. In special cases, however, the following tables may prove of some little value :—

Specific Gravity of Mixtures of Beeswax and Paraffin Wax (*Wagner*)[3]

Beeswax.	Paraffin Wax.	Specific Gravity.
Per cent.	Per cent.	
0	100	0·871
25	75	0·893
50	50	0·920
75	25	0·942
80	20	0·948
100	0	0·969

[1] *Chem. Zeit.*, 1903, 753.
[2] *Journ. Phys. Chem. Soc. Russ.*, 1905 (37), 318.
[3] *Zeitschr. f. analyt. Chem.*, 5, 280.

Specific Gravity of Mixtures of Beeswax and Ceresin (Dieterich) [1]

Yellow Wax.	Yellow Ceresin.	Spec. Grav. of Mixture.	White Wax.	White Ceresin	Spec. Grav. of Mixture.
Per cent.	Per cent.		Per cent.	Per cent.	
100	0	0·963	100	0	0·973
90	10	0·961	90	10	0·968
80	20	0·9575	80	20	0·962
70	30	0·953	70	30	0·956
60	40	0·950	60	40	0·954
50	50	0·944	50	50	0 946
40	60	0·937	40	60	0,938
30	70	0·933	30	70	0·934
20	80	0·931	20	80	0·932
10	90	0·929	10	90	0·930
0	100	0 922	0	100	0·918

Considerable quantities of added ceresin and paraffin wax may be detected by the determination of the unsaponifiable matter, *i.e.* alcohols + hydrocarbons. (It has been pointed out already that the unsaponifiable portion must be determined with certain precautions which are detailed in Vol. I. Chap. VI.) It should be borne in mind that the amount of "unsaponifiable" in different beeswaxes varies within somewhat wide limits. The numbers given in the table of characteristics fluctuate between 52·38 and 55·58. In the examination of 21 samples of beeswax, *Werder* [2] arrived at numbers lying between 48·55 and 53·08 per cent. In view of the tediousness of this process, and the uncertainty of the conclusions to be derived therefrom, it cannot be recommended for the quantitative estimation of added ceresin or paraffin wax, unless it be corroborated and supplemented by other tests. For *Ley's* method cp. Vol. I. p. 602.

The proportion of total hydrocarbons in beeswax is accurately determined by *A. and P. Buisine's* process (Vol. I. Chap. IX.). 2 to 10 grms. of the sample are heated with potash-lime to 250° C., the residue is powdered, and extracted in a Soxhlet extractor with dry ether or dry petroleum ether. The extract is filtered, if necessary, the solvent evaporated off, and the residue dried and weighed. The proportion of hydrocarbons in genuine yellow beeswax varies, according to *Buisine* from 12·7 to 13 per cent, and according to *Kebler*, from 12·5 to 14·5 per cent.

Adulteration with 3 per cent of foreign hydrocarbons can thus be detected, as an easy calculation will show. The liberated hydrogen may also be measured and calculated to melissyl alcohol. 1 grm. of pure beeswax should yield from 53·5 to 57·5 c.c. of hydrogen, corresponding to 52·5-56·5 per cent of melissyl alcohol. In case the determination of the latter be not required, the apparatus for collecting and measuring the gas need not be employed.

More recent determinations by *Ahrens and Hett* have, however shown that the amount of hydrocarbons in beeswax may rise as high

[1] Wagner's *Jahresbericht*, 1882, 1028.   [2] *Chem. Zeit.*, 1900, 967.

as 17·3 per cent (cp. table, p. 900), so that the certainty afforded hitherto by *Buisine's* test for the detection of 3 per cent of hydrocarbons becomes somewhat illusory (cp. also proportion of hydrocarbons in Ghedda Waxes, p. 900).

For some alterations proposed by *Ahrens and Hett* in *Buisine's* arrangement of apparatus, the reader may be referred to the original paper, and it need only be pointed out that for the successful carrying out of *Buisine's* test the potassium hydrate should not be finely powdered, since a fine powder is apt to form lumps when the wax is poured over it. Thus unattacked wax may rise in the tube and escape decomposition.

Detection of Rosin.—The presence of rosin is detected with certainty by the *Liebermann-Storch* colour test. In the case of a dark coloured wax it is advisable to extract the wax with alcohol, and test the residue obtained after evaporating the alcohol. If a 50 per cent alcohol be used and the alcoholic solution be filtered in the cold, any stearic acid present is not extracted. Approximately quantitative results are therefore obtainable if the residue left after evaporating off the 50 per cent alcohol be weighed. More accurate results are arrived at by determining (by *Twitchell's* method) the rosin in the alcoholic extract.

Detection of Spermaceti.—Spermaceti does not affect the acid value (cp. table, p. 907). If considerable quantities of spermaceti be present in beeswax as the only foreign wax, its presence would be detected, and its quantity can be ascertained approximately, by acetylating the isolated unsaponifiable matter. In more complicated cases the alcohols must be examined thoroughly by the methods given in Vol. I. Chap. IX. The quantity of spermaceti can then be derived from the quantity of palmitic acid obtained by the conversion of cetyl alcohol into this acid (cp. Vol. I, Chap. IX.). Such elaborate methods must be especially resorted to in the case of cerates and of wax polishes (see Vol. III. Chap. XVI. Cp. also "Beeswax Candles," Vol. III. Chap. XVI.).

Detection of Carnaüba Wax.—Considerable quantities of carnauba wax may be detected qualitatively by the refractometric test and the chloroform test (see p. 902). The best preliminary method, however, is, in the absence of mineral waxes and insect wax, *Weinwurm's* test, as the author has ascertained by experiments in his laboratory. According to *Berg*, mixtures of beeswax and carnaüba wax commence to melt at 68°-70° C., and are not completely melted at 79°-80° C. From the "ratio number" of the wax conclusions can be drawn as to the presence of carnaüba wax, provided other adulterants which influence the ratio number in the same manner be absent. If they be present, a thorough examination of the neutral esters is required. The quantitative determination of carnaüba wax in beeswax is a very difficult problem, and can only be solved with sufficient accuracy by an exhaustive examination of both the free and combined fatty acids, and of the alcohols by the acetylating and potash-lime processes, described Vol. I. Chap. IX.

Detection of Insect Wax.—As a preliminary test for the detection of insect wax, in the absence of mineral waxes and carnaüba wax, the *Weinwurm* test can be recommended. If insect wax be the only

lulterant, then its presence will be detected by an abnormally high ratio number." It has been pointed out above (p. 917) that in a mple so adulterated the iodine value 11·5 was found. As insect wax ight to have lowered the iodine value of the adulterated sample nsiderably, some other foreign substance must have been added erilla oil ?). It is evident that the detection of insect wax offers fficulties similar to those experienced in the search for carnaüba wax. doubtful cases the problem can only be solved by a thorough exami- ation of the neutral esters.

Detection of Wool Fat and Wool Wax.—The presence of wool fat or ool wax is best recognised by testing the alcohols for cholesterol or ocholesterol. As I have shown (Vol. I. Chap. IX.) that cholesterol n be recovered almost completely from the potash-lime used in *uisine's* process, the safest plan is to convert the alcohols into acids, nd to examine the extracted hydrocarbons for cholesterol.

In addition to the adulterants enumerated above, there would also ave to be considered as a possible adulterant *Montanwax* (see Vol. III. hap. XVI.). Methods for its detection have not yet been worked out p. below).

The author applies in a thorough examination of a sample of beeswax ie following tests in the order enumerated here :—

Acid value, saponification value, specific gravity, melting point ; per- entage of unsaponifiable matter, iodine value, determination of glycerin, Veinwurm test, extraction with alcohol and examination of the extracted lty acids, percentage of fatty acids yielding respectively easily soluble and paringly soluble soaps (by a method applied first in the examination of ool wax ;* [1] see Vol. I. Chap. XI.).

The **unsaponifiable matter** is then further examined for *melting oint, increase on acetylation, appearance of the acetylated mass in the hot rponification value of the acetate,* and, if need be, conversion of the lcohols into fatty acids.

Each portion of the **fatty acids** isolated from the easily soluble and paringly soluble soaps is examined separately for *melting point* and *oleular weight.* The quantity of fatty acids isolated from the *spar- ugly* soluble soaps is as a rule contaminated with stearic acid, etc., nd cannot be calculated direct as cerotic acid ; it is therefore advisable o treat these fatty acids with 80 per cent alcohol (see p. 919) in order o remove acids of a lower melting point than that of cerotic. Any " montanic " acid due to the presence of montanwax, as also carnaübic cid from carnaüba wax, would be found with the " cerotic " acid. Nor should the whole amount of " cerotic " acid be calculated to)eeswax, unless the absence of insect wax has been ascertained. By applying these tests in a systematic fashion, and by calculating that omposition which satisfies best the analytical data, the many errors nherent to the methods can be eliminated to a very large extent, so hat the final results may approximate to the true composition within } to 5 per cent.

[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 134 ; 1896, 14.

If the acid value and saponification value found in the actual sample
he diminished by those amounts which are due to added free fatty acids
and saponifiable substances respectively, the calculated 'acid and
saponification values may as a rule be looked upon as due to beeswax
only.   If a " normal " heeswax had been used in the production of the
sample, the ratio of acid value to saponification value will then be ahout
20 : 95 for a crude wax, and about 25 : 95 for a bleached wax.   In case
a sample consists of Indian or Chinese or Japanese beeswax only (see
table, p. 914), its abnormal acid and saponification values will define
its origin, if no adulterant can he detected.   In that case, confirmation
may be found in the consistence, these waxes being much softer than
African waxes ; they are further characterised by a peculiar aromatic
odour.   It would he impossible to condemn these waxes, inasmuch as
they are the genuine secretion of the bee (see abovc), although not that
of *Apis mellifica*.   This point deserves the serious attention of the
analyst, as the quantities of heeswax exported from India alone are not
inconsiderable.   This may be gathered from the following tahle :—

Quantity of Beeswax exported from the Whole of India

					Cwts.
1878–79	.	.	.	.	3,311
1880–81	.	.	.	.	6,592
1885–86	.	.	.	.	5,635
1887–88	.	.	.	.	5,989
1888–89	.	.	.	.	4,573
1889–90	.	.	.	.	4,222
1890–91	.	.	.	.	6,514
1891–92	.	.	.	.	5,814
1892–93	.	.	.	.	4,667
1893–94	.	.	.	.	5,816
1894–95	.	.	.	.	7,487
1895–96	.	.	.	.	5,882
1896–97	.	.	.	.	3,142
1897–98	.	.	.	.	3,537
1898–99	.	.	.	.	4,846
1899–1900	.	.	.	.	5,787
1900–1	.	.	.	.	5,059
1901–2	.	.	.	.	4,139
1902–3	.	.	.	.	4,481
1903–4	.	.	.	.	6,685
1904–5	.	.	.	.	6,941
1905–6	.	.	.	.	8,593
1906–7	.	.	.	.	8,162
1907–8	.	.	.	.	5,120
1908–9	.	.	.	.	4,671
1909–10	.	.	.	.	6,998
1910–11	.	.	.	.	8,552
1911–12	.	.	.	.	12,527

The production of 1902–3 came from Bengal (3020 cwts.), Bombay
(762 cwts.), Madras (427 cwts.), Burma (230 cwts.), and Sind (42 cwts.) ;
and of 1911–12 from Bengal (7305 cwts.), Bomhay (3156 cwts.), Madras

(1343 tons), and Burma (723 cwts.) ; the chief exports in 1902–3 were to Straits (2062 cwts.), United Kingdom (1313 cwts.), Germany (534 cwts.), Ceylon (312 cwts.), France (176 cwts.), United States (67 cwts.),[1] Java, Belgium, and Mauritius (17 cwts.), and in 1911–12 to Straits (3932 cwts.), United Kingdom (2074 cwts.), Germany (3458 cwts.), Ceylon (125 cwts.), France (334 cwts.), Portuguese East Africa (500 cwts.), Belgium (579 cwts.). These beeswaxes differ from the wax of the domesticated bee by containing a smaller amount of free cerotic acid and hydrocarbons, and inferentially by a larger proportion of "myricin." But as they are used in industry, moreover as they can be bleached successfully, and therefore enter largely into the composition of candles, the greatest caution is required in judging a beeswax which consists of a mixture of " normal " and " abnormal " beeswaxes. To emphasise this point, the following table, due to *Buchner*,[2] may be reproduced :—

Calculated Acid and Saponification Values of Mixed " Normal " and " Abnormal " (Ghedda) Beeswaxes

Ghedda Wax. Per cent	"Normal" Beeswax Per cent	Acid Value.	Saponification Value
10	90	18·5	94·8
20	80	17·6	95·2
30	70	15·5	94·5
40	60	14·1	94·4
50	50	12·6	94·2
60	40	11·1	94·1
70	30	9·7	94·0
80	20	8·2	93·8
90	10	6·7	93·7

It will thus be seen that if such mixtures be under examination the analysis of beeswax offers the greatest difficulties. In such a case only the rigorous elimination of all possible adulterants by an exhaustive search can lead to decision.

The bleached East Indian wax is frequently adulterated (in Calcutta) with bleached wax.

The chief uses of beeswax are for making candles (Russia alone consumes about 6500 tons per annum), wax polishes, and modelling wax.[3] Smaller quantities are employed in the manufacture of cosmetics,

[1] The total import of beeswax into the United States amounted in 1905–6 and 1906–7 to 5228 and 8200 cwts. respectively, and in 1911 and 1912 to 8061 and 9613 cwts. respectively.

[2] Buchner, *Chem. Zeit.*, 1906, No. 43 ; *Chem. Zeit.*, 1908, No. 7.

[3] For modelling flowers, fruits, illustrations of botanical specimens, and finest works of art pure beeswax is used, or at most a small quantity of lard or olive oil is added, in order to make the wax more pliable. Some modelling waxes consist of pure beeswax and a few per cent of oil of turpentine. Modelling wax in Germany is usually prepared from 5 parts of beeswax, 1 to 1½ parts of oil of turpentine, and a ¼ to ½ part of sesamé oil.

cerates, ointments, encaustic paints, lithographic ink,[1] and for galvano-plastic purposes.

Reliable statistics as to the world's production are not available, but it may be stated that the import of beeswax into Germany in the year 1902 amounted to 1421 tons, and in 1911 and 1912 to 2666 and 2999 tons respectively.

Waxes used in pharmaceutical practice must conform to the speci-fications of the various pharmacopoeias, which up till now require numbers corresponding to " normal " waxes ; hence Chinese, Japanese, and East Indian (Ghedda) waxes and mixtures thereof with " normal " waxes are not tolerated by the specifications of the pharmacopoeias.

Isolated data are the following :—France produces about 2500 tons of beeswax, and exported in 1913 239 tons, Russia about 2400 tons, Madagascar from 150 to 200 tons, and Algeria from 100 to 150 tons per annum.

The value of the total export of beeswax from the Gambia Pro-tectorate and colony was in 1911 and 1912 £1514 and £1164, and that from Abyssinia £39,462 and £22,576. From Tangier the exports amounted in 1912 to 295 cwts, the whole of which went to Germany.

RUMP GLAND WAX

French—*Cire des glandes anales des oiseaux.*   German—*Bürzel-drüsenwachs.*   Italian—*Cera di codrione degli uccelli.*

This wax occurs in the rump glands of birds, together with animal fat. The following characteristics of the wax have been given by *Röhmann.*[2]

Acid value	.	.	.	136-175
Iodine value		.	.	15·5-26·5

The wax contains up to 43·5 per cent of octodecyl alcohol. Chol-esterol is absent. The saturated acids are stated to exhibit optical activity.

SPERMACETI (CETIN)

French—*Blanc de baleine, Cétine.*   German.—*Walrat.*
Italian—*Spermaceto.*

For table of characteristics see p. 930.

Spermaceti (cetin) occurs chiefly in the head cavities and in the blubber of the sperm whale, *Physeter macrocephalus* (cp. p. 863), and

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For larger models stearine or rosin, or both, are admixed with bleached wax in definite proportions. Cheap modelling waxes now made for purposes of instruction contain considerable amounts of paraffin wax, and also of sulphur.

[1] Manche, Noclain et Chavet, French patent 397,923.

[2] *Zeit. f. die gesamte Biochemie,* 1904, 111.

the bottlenose whale, *Hyperoödon rostratus*; it has been also found in somewhat smaller quantities in other *cetacea*; it constitutes tho solid portion of dolphin oil (p. 466) and of shark liver oil. The mode of preparing crude spermaceti has been described above, p. 863. Crude sperm oil yields about 11 per cent of spermaceti. The crude spermaceti is melted and boiled two to three hours with a dilute caustic soda lye,[1] containing about 2·5 per cent of caustic soda, and finally washed with water till free from alkali. The clarified oil is then drawn off into flat tin moulds, in which the mass is allowed to crystallise. The cakes are broken up and comminuted to powder, which is pressed in bags in a hydraulic press, first in the cold and then in the hot.

Refined spermaceti forms lustrous, white, translucent, tasteless, and odourless masses with a broad leafy crystalline structure; it is so brittle that it can be rubbed to powder. In the melted state it leaves a grease-spot on paper. It is insoluble in cold 90 per cent alcohol, and sparingly soluble in 96 per cent alcohol; it dissolves, however, easily in boiling alcohol (1 part in 40 parts). On cooling, the bulk separates in a crystalline condition. Spermaceti is readily soluble in ether, chloroform, and carbon bisulphide.

Chemically, spermaceti consists chiefly of cetin,[2] *i.e.* cetyl palmitate. Since the saponification value of pure cetin is 116·9, it is evident that other esters must occur in spermaceti. This is confirmed indirectly by the percentage increase on acetylating the alcohols (see Vol. I. Chap. IX.). The statement [3] that spermaceti contains also glycerides of lauric, myristic, and stearic acids as normal constituents requires confirmation. *Lewkowitsch* [4] found in a commercial sample of the saponification value 122·3, the acetyl value 2·63; this would point to the presence of a small amount of free alcohols. By crystallisation from alcohol pure cetin is obtained.

On examining *commercial* samples, the author found iodine absorptions of 3·52 to 4·09, no doubt owing to small quantities of sperm oil adhering to the spermaceti. The higher iodine values found by *Dunlop*, viz. 5·3-9·33, must be due to some sperm oil having remained behind; this is confirmed by the exceedingly low melting points of the fatty acids which *Dunlop* found, viz. 32 to 40. *Branderhorst* [5] found the iodine value 6·7 for a specimen melting at 44° C. If other iodine-absorbing impurities (tallow) are absent, the proportion of sperm oil may be calculated, adopting 82·5 as its iodine value.

The esters in spermaceti are readily saponified by boiling with alcoholic potash; on diluting the alcoholic solution with water, cetyl alcohol is precipitated.

[1] D. Bridges, English patent 966, 1770.
[2] The requirements of the U.S. Pharmacopoeia appear to correspond rather with the numbers calculated for cetin than those ascertained hitherto for spermaceti; cp. L. Kebler, *Journ. Soc. Chem. Ind.*, 1896, 206.
[3] Heintz, *Liebig's Annal.*, 1854, 92. 291.   [4] *Analyst*, 1899, 321.
[5] *Pharm. Weekblad*, 1909 (46), 1043.

Physical and Chemical Characteristics of Spermaceti

Specific Gravity			Solidifying Point		Melting Point.[1]		Saponification Value	
At °C.		Observer.	°C.	Observer.	°C	Observer.	Mgrms. KOH.	Observer.
15	0·960	Dieterich	43·4-44·2	Rudorff	43·5-44·1	Rudorff	128	Allen
	0·905-0·945	Kebler			45	Barfoed	125·8-134·6	Kebler
60	0·8358	Allen	42·47	Kebler	42·44·5	Kebler	130·6-131·4	Henriques
98·99 (water at 1·5=1)	0·8086-0·812	Allen	41-45·7	Dunlop	41-46	Dunlop	122·7-130·1	Lewkowitsch
(water at 15·5=1)	0·8082-0·816	Kebler	49-43·5	Branderhorst	44	Branderhorst	120·6-129	Dunlop

Physical and Chemical Characteristics of Spermaceti—continued

Iodine Value		Alcohols.[2]		Fatty Acids.		Iodine Value.	
Observer.	Per cent.	Per cent.	Observer.	Per cent.	Observer.	Per cent.	Observer.
Lewkowitsch	3·52-4·09	51·41	Lewkowitsch	53·45	Lewkowitsch	3·8	Lewkowitsch
Dunlop	5·3-9·3	51·56-54·27	Dunlop	49·78-50·58	Dunlop		
Branderhorst	6·7	49	Branderhorst				

[1] The melting point of a specimen of spermaceti melting at 42° C. was raised to 43·5° C., by crystallising twice from alcohol, and by subsequent recrystallisation from ether 5 times to 48·5° C. (Fendler, Chem. Zeit., 1905, 555).

[2] Melting point of the alcohols 46·7° C.(Lewkowitsch); 45° C. (Fendler, Chem. Zeit., 1905, 555); 45·5° to 48° C. (Dunlop). The iodine numbers of the alcohols prepared by Dunlop varied from 2·98 to 6·3

Spermaceti cannot be easily adulterated, as any foreign substance causes it to lose its physical characters, such as transparency and crystalline structure. Genuine samples of commercial spermaceti contain small quantities only of free fatty acids. Thus *Lewkowitsch* found in a commercial sample the acid value 1·35, *Kebler* in the examination of twelve samples of spermaceti acid values ranging from 0·09 to 0·47, and *Dunlop* 0·20 to 0·48.

A higher acid value of a sample would indicate the presence of *stearic acid* or *beeswax*, a high iodine value that of *tallow*. These substances would also be pointed out by abnormal saponification values. They, as also *paraffin wax*, may be identified by the methods described under " Beeswax."

A rapid process for the detection of *stearic acid* [1] is to melt the sample in a porcelain basin, and to stir it well with a few c.c. of ammonia. After cooling, the solidified cake is removed and the aqueous solution acidified, when stearic acid separates. The presence of even one per cent of stearic acid may be thus ascertained.

Spermaceti is employed in the manufacture of sperm candles, some kinds of " beeswax " candles, cerates (see Vol. III. Chap. XV.), and for cosmetic purposes.[2] The alcohols obtained from spermaceti are said to form a useful basis for ointments.[3]

INSECT WAX, CHINESE WAX

French—*Cire d'insectes, Cire de Chine.* German—*Insektenwachs, Chinesisches Wachs.* Italian—*Cera d' insetti.*

For table of characteristics see p. 933.

Insect wax is the secretion of an insect, *Coccus ceriferus*, Fabr., or *Coccus pela*, Westwood.

The larvæ of the insect appear early in the spring on the bark, boughs, and twigs of *Ligustrum lucidum*, Ait. (the " evergreen " tree growing in the Chien-Chang valley, Western China, near the Thibetan frontier), in the form of numerous brown, pea-shaped scales. These scales are gathered by the natives about the end of April, wrapped carefully in packages (each containing about 1 lb.), so as to protect the larvæ from the heat whilst these packages are being carried to Chia-ting, the centre of the insect wax industry, a distance of about 200 miles from the Chien-Chang valley. (In order to prevent the premature development of the larvæ, the packages must be kept as cool as possible and, therefore, the carriers only travel by night.) Each package is subdivided into smaller packages, wrapped in leaves, and suspended

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[1] *Les Corps gras industriels*, 13. 207.
[2] *Zeitschr. f. angew. Chem.*, 1905, 1760.
[3] A mixture of these alcohols with vaseline is sold under the fancy name " Cetaceum "
(Blatz, *Pharm. Zentralbl.*, 1908, 537).

under the branches of a species of ash (most likely *Fraxinus chinensis*), after holes have been made in the leaves which cover the larvæ. On emerging from the scales, the insects creep up the branches to the leaves of the tree, among which they remain thirteen days ; they then descend to the branches and twigs, where the insect wax is secreted.' The first appearance of the wax on the undersides of the boughs and twigs resembles snow ; it gradually spreads over the whole branch to the depth of about a quarter of an inch. Three months after placing the insects on the tree the branches are cut off, and as much wax as possible is removed by hand. In order to recover a further quantity the branches are boiled with water. The larvæ are thereby destroyed, and hence fresh scales must be brought the following year for another crop of wax. One pound of scales is stated to produce four to five pounds of wax (*Hosie*).

The annual production of insect wax varies greatly with climatic conditions, as wind and rain act destructively on the insects.

Insect wax has a yellowish-white colour ; it is odourless and tasteless, has a lustrous appearance and a crystalline structure, resembling in these respects spermaceti ; it is, however, more fibrous and considerably harder, and can be powdered more easily.

This wax is very slightly soluble in alcohol and ether, but easily soluble in benzene, from which it can be obtained in a crystalline form. It consists chiefly of ceryl cerotate, $C_{26}H_{53} . C_{26}H_{51}O_2$, which can be readily isolated from the wax by repeated crystallisation from petroleum ether (boiling point 115°-135° C.). Since the theoretical saponification value of ceryl cerotate is 73·8, other esters are evidently admixed with the ceryl cerotate, as the saponification values of commercial samples are considerably higher. Owing to the separation of potassium cerotate during saponification and titration, low saponification values were found by earlier observers ; such lower numbers are omitted here. A commercial sample of Chinese wax examined by the author absorbed 1·4 per cent of iodine. Another sample had the acid value 1·5. In the *Weinwurm* test (see p. 921) Chinese wax behaves like a beeswax adulterated with paraffin wax (*Lewkowitsch*).

Insect wax is used in China and Japan for making candles, for polishing furniture and leather, and as a sizing material for paper, silk, and cotton goods. On account of its extensive use in China and Japan it is not largely exported to Europe.[1]

[1] *Journ. Soc. Chem. Ind.*, 1897, 685.

[TABLE

Physical and Chemical Characteristics of Insect Wax

Specific Gravity			Solidifying Point		Melting Point		Saponification Value		Fatty Acids		Alcohols		Iodine Value	
At °C.		Observer	°C.	Observer	°C.	Observer	Mgrms. KOH	Observer	Per cent.	Observer	Per cent.	Observer	Per cent.	Observer
15	0·970	Allen	80·5-81	Allen	80·5-81	Allen	93	Henriques	51·54[1]	Lewko-witsch	49·51	Lewko-witsch	1·4	Lewko-witsch
99 (water 15·5=1)	0·810	,,			81·5-83	Henriques	80·5	,,						
							91·65	Lewkowitsch						
							80·4	,,						

[1] Melting point of the fatty acids 92·2° C. (Lewkowitsch).

PSYLLA WAX [1]

This wax is secreted by *Psylla alni*, an aphide living on the leaves of *Alnus incana*. It is obtained by extracting the insects first with hot ether, in order to remove glycerides, and finally with hot chloroform.

The wax is insoluble in hot ether, and only sparingly soluble in cold chloroform, but readily soluble in hot chloroform and in benzene. It crystallises in needles of silky lustre, melting at 96° C.

Psylla wax is the psyllostearylic ester of psyllostearyl alcohol (see Vol. I. Chap. III.). The hydrolysis of the wax is stated to be effected less expeditiously by alcoholic potash than by hydrobromic acid.[2]

Sundwick [1] states that the alcohol from psylla wax does not decompose when heated with an excess of caustic potash, even when heating is continued until the larger part of the alcohol is volatilised. On heating with soda-lime, however, besides hydrogen and water, an acid melting at 94° is obtained (Psyllostearylic acid). This shows a marked difference from the alcohol obtained from bumble bee wax.

WAX FROM TUBERCULOSIS BACILLI

French—*Cire de bacille tuberculeux;* German—*Tuberkel-bacillenwachs.* Italian—*Cera di tubercoli.*

On extracting dried tuberculosis bacilli with chloroform, *Kresling* [3] obtained a fatty substance consisting, according to his statements, of :— free fatty acid, 14·38 per cent ; neutral fats and fatty acid esters, 77·25 per cent ; lecithin, 0·16 per cent ; water-soluble substances, 0·73 per cent. From the " fatty acid esters," 31·9 per cent of alcohols melting at 43·5° C. were obtained. The total fatty matter had the following characteristics :—

Melting point	.	.	.	.	46° C.
Acid value	.	.	.	.	23·08
Reichert-Meissl value	.	.	.	.	2·00
Fatty acids + unsaponifiable	.	.		74·24 per cent
Saponification value	.	.	.	.	60·70
Iodine value	.	.	.	.	9·92

The fatty substance seems to be a wax,[4] which is only saponified with great difficulty, for a similar preparation obtained by *Bullock and Macleod* by extracting dry tubercle bacilli with *Aronson's* mixture (alcohol and ether containing 1 per cent of hydrochloric acid), furnished,

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[1] *Zeitschr. f. phys. Chem.,* 1901 (32), 355 ; *ibid.,* 1911, 455.

[2] *Ibid.,* 1908 (54), 255.

[3] "Über die Fettsubstanz der Tuberkelbacillen," *Centralbl. f. Bakteriol.,* 1901, xxx. 897.

[4] Cp. Ritchie, *Journ. Path. and Bact.,* 1905, 334.

after saponification with sodium alcoholate, a substance which on examination by *Lewkowitsch* [1] gave the following numbers :—

Iodine value	9·39
Saponification value	49·40
Melting point	44·4° C.
Increase of weight on acetylating	1·2 per cent
Saponification value of acetylated product	69·0

These numbers show that a considerable amount of the wax had escaped saponification.

Aronson [2] states that the acid value in hot alcoholic solution was 40·8. · The alcohol-soluble portion contains a large proportion of phosphorus-containing compounds resembling lecithin. *Aronson* further states that the insoluble portion was a higher alcohol which was not a cholesterol. This is confirmed by *Panzer* [3] who extracted the dried bacilli with ether. This extract on examination by the digitonin test showed no indication of the presence of cholesterol. *Fontes* [4] states that he has found indications of palmitic acid.

The manufacture of the wax (" fatty substance ") from tuberculosis bacilli and other micro-organism, especially from *Streptothrix leproides*, and its employment for medicinal purposes [5] has been patented by *Kalle & Co.*,[6] and also *Meister, Lucins, and Brüning*.[7]

[1] " Chemical Constitution of the Tubercle Bacillus," by W. Bullock and J. J. R. Macleod, *Journal of Hygiene*, 1904 (iv.), 7.

[2] *Berliner klin. Wochenschr*, 1910, No. 35, 13.

[3] *Zeitschr. f. physiol. Chem.*, 1912, 78, 414.

[4] *Zentralbl. f. Bakter. u. Parasitenk*, 1909, 317.

[5] Cp. Deycke (Pasha) and Reschad (Bey), *Deutsche medic. Wochenschr.*, 1907, 89.

[6] English patent 26,077, 1906 ; German patents 193,883, 199,200 ; English patent 27,383, 1907 ; German patent 201,989. An addition to German patent 199,200 claims as solvents (for the extraction of the "fatted substance ") benzaldehyde, benzyl alcohol salicyl aldehyde, cinnamic aldehyde, and benzoyl chloride. Cp. also *Zeitschr. f. angew. Chem.*, 1909, 102 ; and German patents 212,350, 212,830, 213,393, 214,071 (Kalle & Co.).

[7] English patent 23,022, 1911 ; cp. German patent 239,560.

Lesser Known Animal Waxes

Wax from	French	German	Italian	1 Number of Samples.	2 Specific Gravity at 15°C.	3 Melting Point °C.	4 Butyro-refractometer "Degrees" observed at 84°C., calculated to 40°C.	5 Acid Value.	6 Saponification Value.	7 Difference, 5-4.	8 "Ratio Number."	8 Iodine Value.	9 c.c. norm. KOH required for Acids soluble in 80 per cent Alcohol.	10 Hydrocarbons. Per cent.	Observer.
Bumble bee[1] from Bombus terrestris, B. muscarum, B. lapidarius — Max.	Cire de bourdon	Hummel-bienen-wachs	Cera di cata-brone	19	...	63·0	51·6	19·39	95·90	76·65	4·00	16·10	9·18	...	Berg
,, Mean					...	62·0	50·0-51·0	19·0-	95·0-	76·0-	3·95-	15·8-	5·0-7·0	...	Berg
,, Min.				...	0·973	62·0	49·5	19·2	95·5	76·5	4·0	15·9	4·92	...	Berg
								18·41	92·12	73·71	3·93	15·76		25·1	Ahrens Hett
								7·8	48·3	40·5	5·2	...		...	
Cicade wax—I.	Cire de cicade	Cicaden-wachs	Cera di cicale	...	0·965	...	...	7·8	95·9	88·1	11·29	...	...	10·6	,,
,, II.				...	0·965	...	...	7·3	97·95	90·65	12·41	...	...	8·2	,,
Ceroplastes ceriferus[2] — Expressed				...	1·04	60	...	...	...	...	...	...	...	...	,,
Extracted				...	...	54	...	...	...	...	...	...	...	...	
Ceroplastes rubens — Expressed				...	1·03 at 23°C.	60	...	...	...	...	...	...	...	...	,,
Extracted				...	...	55 38	...	...	...	...	...	...	...	...	
Axin wax from Coccus axin[3]	Cire d'axin	Axin-wachs	...	...	...	...	...	...	...	...	...	...	...	...	Bocquillon

Cochineal wax from *Coccus cacti* consists of cocceryl coccerate to an extent of from 0·5 per cent (in Zacatille cochineal) to 4·2 per cent (in Granilla cochineal). From "silvery cochineal" Huerre[4] extracted about 7·8 per cent of a fat by means of ether, in which the cochineal wax is practically insoluble. This fat contained only 3 per cent of unsaponifiable matter, and had an iodine value of 50. The fatty acids consisted of oleic, linolic, and myristic acids.

[1] This wax has a very unpleasant smell, which it has not yet been possible to remove; it cannot therefore be used as an admixture to genuine beeswax (R. Berg, *Chem. Zeit.*, 1907, 538).

[2] This wax is known in commerce as "Arjun wax." The "Mission forestière de l'Afrique occidentale française" found the Ceroplastus insect living on two species of acacia, which are widely distributed on the banks of the Senegal river.

[3] An insect living on *Spondias lutea, Zanthoxylum Clava-Herculis, Z. Pentanome* in Mexico.

[4] *Journ. Pharm. Chim.*, 1911, 56.

INDEX OF BOTANICAL NAMES